THE 1,2-PHOTOAROMATIZATION REACTION

A VERSATILE ROUTE TO HIGHLY STRAINED RING SYSTEMS

by

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Except as herein stated, this Thesis contains no material submitted for the award of any other degree or diploma in any University, and to the best of my knowledge, contains no copy or paraphrase of material written or published, except when due reference is included in the text.

Eric E Nunn

(Eric E. Nunn)

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ABSTRACT

Hexakis(trifluoromethyl)benzvalene, prepared by irradiation of the corresponding benzene, has been shown to react with cyclobutadiene, affording a mixture of *syn* and *anti* 1:1 adducts. Heating these adducts at 240° results in isomerization to 1,2,3,4,5,6-hexakis(trifluoromethyl)tetracyclo[4.4.0.$0^{2,4}$.$0^{3,5}$]deca-7,9-diene, whose behaviour under photolytic and pyrolytic conditions is discussed.

The 1,2-photoaromatization reaction has been applied to the synthesis of 1,2-dimethoxycarbonyl-1,2-diazet-3-ine, a novel heterocycle for which naive application of the Hückel $(4n + 2)\pi$ rule would predict aromatic character. Simple HMO calculations are performed, and the properties and structure of the ring system discussed.

The 1,2-photoaromatization reaction has been successfully applied to the synthesis of benzo- and dibenzobarrelenes. Modification of the approach has allowed preparation of dihydrobarrelenes, though extension to the parent barrelene system was frustrated by competing reactions.

2,3,4,5-Tetrachlorobicyclo[4.2.0]octa-2,4,7-triene has been synthesized by the photochemical decarbonylation of *exo*- and *endo*-1,6,9,10-tetrachlorotricyclo[4.2.2.$0^{2,5}$]deca-3,9-dien-7,8-dione. The thermal and photochemical transformations of this compound are discussed, with special reference to the orbital-symmetry requirements of the processes involved.

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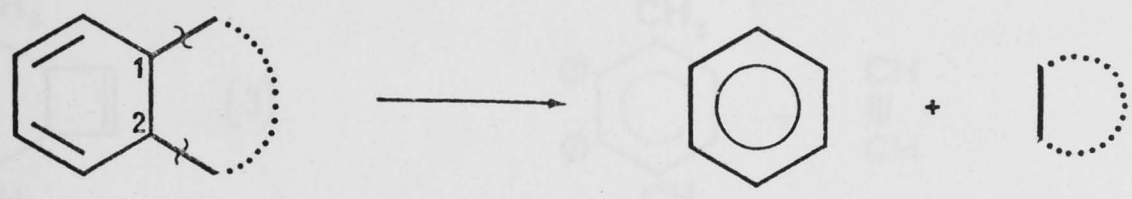
INTRODUCTION

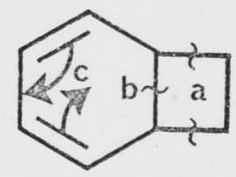
THE 1,2-PHOTOAROMATIZATION REACTION

A 1,2-photoaromatization reaction has been defined[1] as an ultra-violet light induced fragmentation in which one portion of a molecule (containing the energy absorbing chromophore) is converted to an aromatic hydrocarbon, while the other fragment remains structurally intact. (The prefix 1,2- refers to the relative positions of the two σ bonds involved in the fragmentation).



Thus on irradiation of bicyclo[4.2.0]octa-2,4,7-triene (1), photoaromatization would lead to benzene and acetylene - and these are the observed products[2]. A number of substituted derivatives have also been investigated, and these are collected in Table 1.

Considering photochemical excitation of the bicyclo[4.2.0]octa-2,4-diene system, three intramolecular processes might be envisaged: a) photoaromatization*; b) con-rotatory ring-opening; and c) 4π disrotatory cyclization. These are illustrated above. The last mentioned process, though common in other cyclic 1,3-dienes[8], has not



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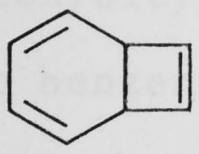
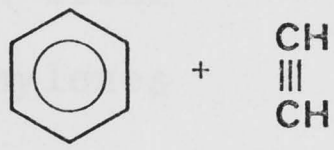
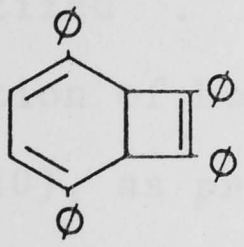
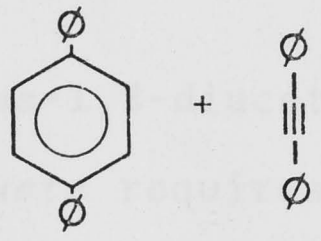
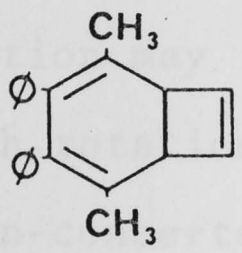
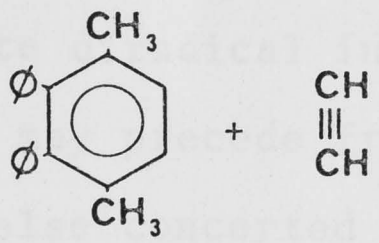
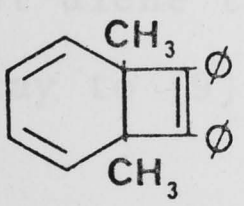
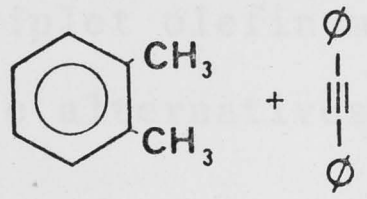
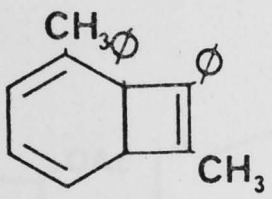
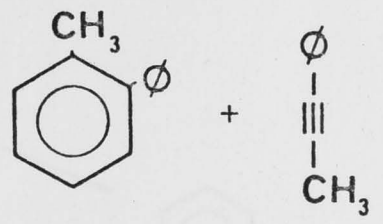
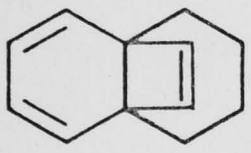
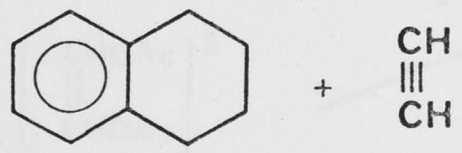
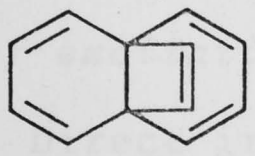
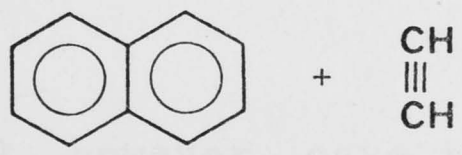
* Aromatization can also occur through loss of hydrogen, though this has been only rarely observed[7].

TABLE 1

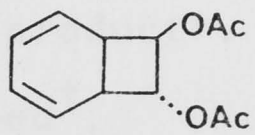
Photolyses of Bicyclo[4.2.0]octa-2,4,7-trienes.

Derivative		Photoproducts	Reference
	(1)		2
	(2) *		3
	(3)		4
	(4)*		4
	(5)*		4
	(6)		5
	(7)		6

* In these cases, the bicyclooctatriene is the presumed intermediate on photolysis of the corresponding cyclooctatetraene.

previously been observed* in bicyclo[4.2.0]octa-2,4-diene systems.

Photoaromatization in this system, if concerted, would be a symmetry-allowed excited-state process[9]. However, photochemical fragmentation of *trans*-7,8-diacetoxybicyclo[4.2.0]octa-2,4-diene (8) to benzene and diacetoxyethylenes has been shown to be triplet-sensitized[10]. Moreover, the isolation of both *cis*- and *trans*-1,2-diacetoxyethylenes, (9) and (10), as *primary photoproducts* requires a mechanism which can account for this loss of stereochemistry. Thus the reaction may involve a discrete diradical intermediate, in which rotation about a σ bond may precede fragmentation (i.e., a non-concerted process), or else concerted cleavage of the triplet diene to benzene and triplet olefin may occur, followed by decay to (9) and (10). These alternatives are illustrated below.



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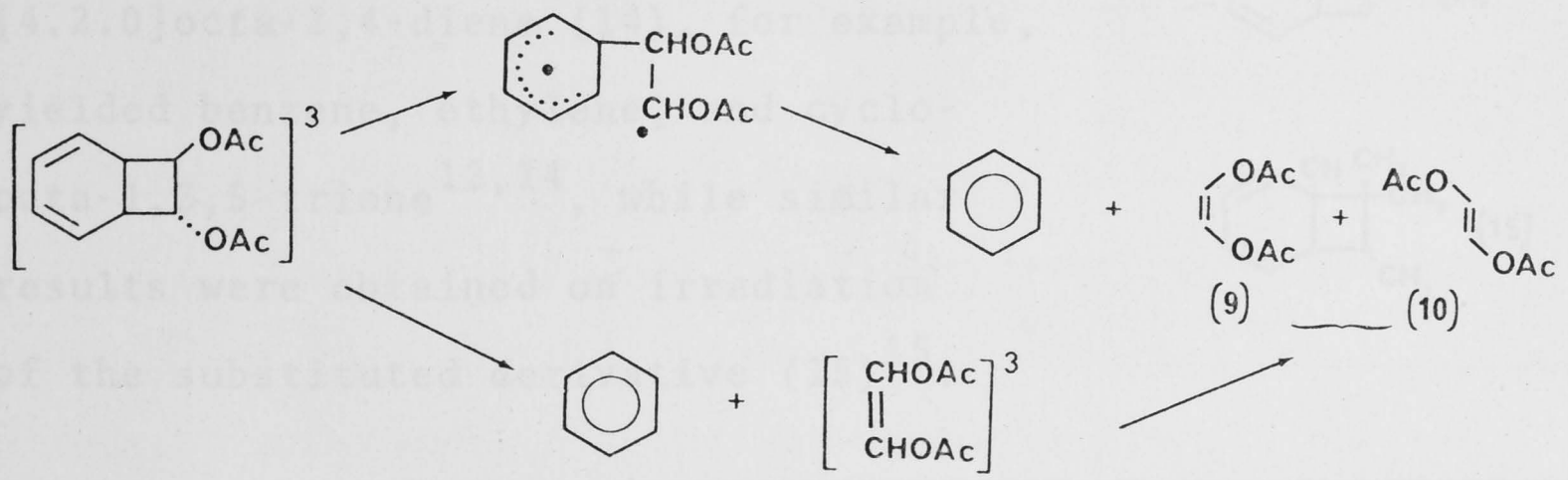

Which mechanism operates then, depends on the *timing of the loss of excitation energy*[10].

Direct irradiation of (8), however, gave instead of

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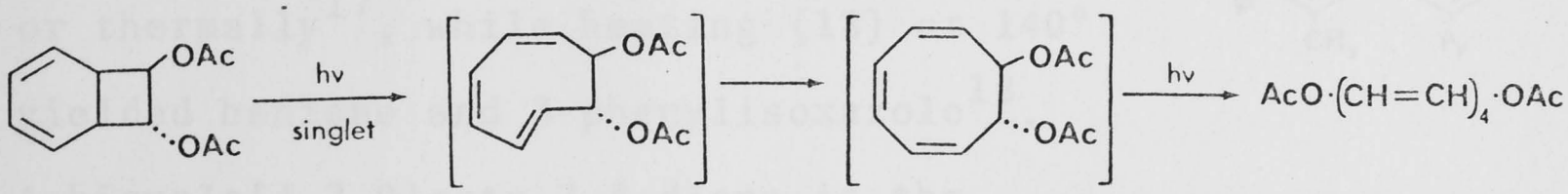
* See however Section C.

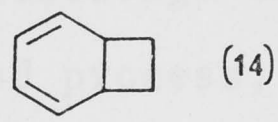
diacetoxyethylenes[10], the diacetoxytetraene (13)[11]. A mechanism which does not contravene orbital symmetry requirements[9] involves excited-state conrotatory ring-opening leading to the highly strained *trans,cis,cis*-cyclooctatriene (11), followed by isomerization to (12). Disrotatory ring-opening of (12) would then give the observed product*. The intermediacy of (11) has never been established†.



(8) (11) (12) (13)

This mode of cleavage has been suggested[10] to occur from the excited singlet state, in accord with observations on the related photochemical ring-opening of cyclohexa-1,3-diene to hexa-1,3,5-triene[13].

In related bicyclo[4.2.0]octa-2,4-diene systems, both photoaromatization and ring-opening reactions have been observed to occur concurrently. Irradiation of bicyclo-[4.2.0]octa-2,4-diene (14), for example, yielded benzene, ethylene, and cyclo-octa-1,3,5-triene[12,14], while similar results were obtained on irradiation of the substituted derivative (15)[15].



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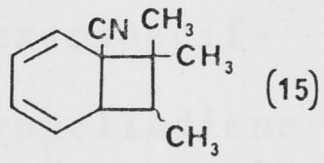

(15)

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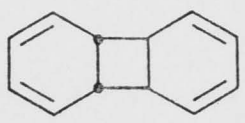
* The stereochemistry of (13) was not determined, but on the basis of the above mechanism, initial formation of the *cis, cis,cis,trans* isomer would be predictable.

† Spectroscopic evidence for a similar transient species has been obtained on irradiation of cycloocta-1,3,5-triene in an inert vapour matrix at 20°K[12].

In some instances, aromatization occurs both thermally and photochemically. Thus, low temperature irradiation of hydrocarbon (16), or warming above 30°, caused facile cleavage to two molecules of benzene[16]. The related dihydropyridazine derivative (17) underwent a similar cleavage either photochemically or thermally[17], while heating (18) at 140° yielded benzene and 3-phenylisoxazole[18]. A bicyclo[4.2.0]octa-2,4-diene is the presumed intermediate in the formation of benzene and cyclobutene on pyrolysis of the tetracyclodecene (19)[19].



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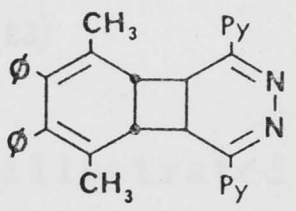

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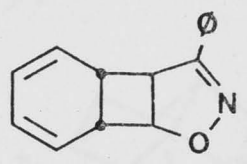

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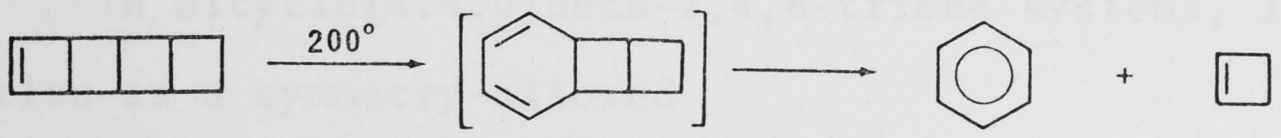
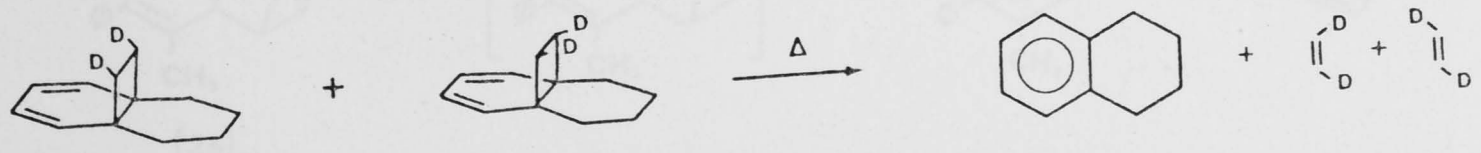


(19)

It has recently been shown that thermal cleavage of bicyclo[4.2.0]octa-2,4-dienes is a non-concerted process, proceeding through a diradical intermediate of sufficient lifetime to allow bond rotation and loss of stereospecificity[20]. Thus pyrolysis of the dideuterated propelladiene derivatives (20) and (21) yielded both *cis*- and *trans*-dideuterioethylenes (66% and 34% respectively).

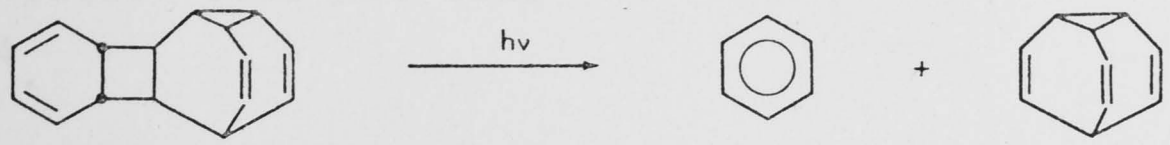


(20) (21)

Similar results were obtained with 11-methoxy derivatives[20].

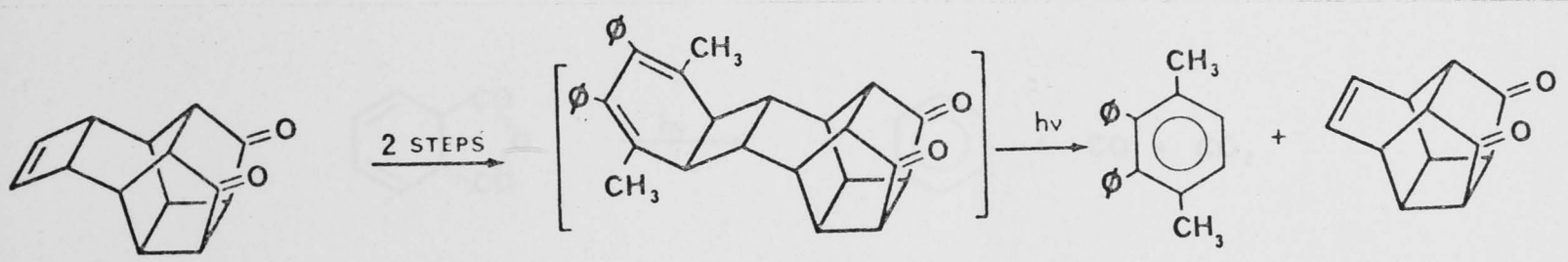
The first synthetic application of the 1,2-photo-

aromatization reaction was Schröder's elegant synthesis of bullvalene (23) by irradiation of the cyclooctatetraene dimer (22)[21].



(22) (23)

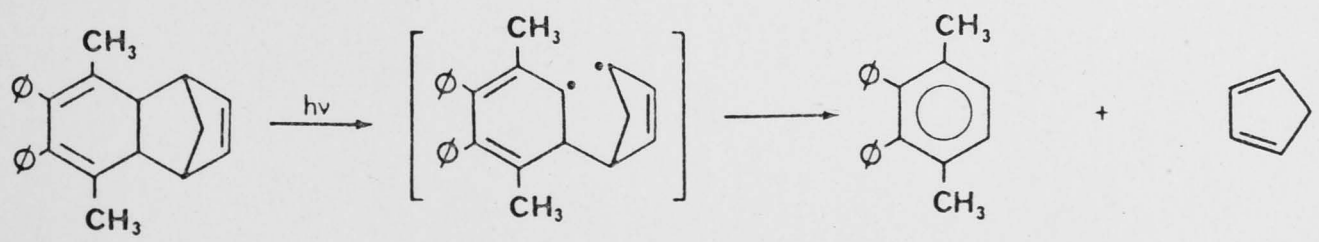
Recently, Warrener *et.al.*[1] have further illustrated the synthetic potential of the reaction by conversion of the readily available cyclobutene (24) to olefin (25).



(24) (25)

In bicyclo[4.4.0]deca-2,4,8-triene systems, 1,2-aromatization is a symmetry-allowed thermal process[9] and numerous examples have appeared in the literature[22]. Most notable is the application to the synthesis of isobenzofuran[23].

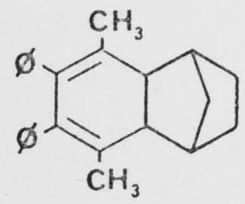
However, the reaction has also been shown to occur under photochemical conditions, presumably by a non-concerted pathway[24]. This is best illustrated by considering triene (26) in which homolytic cleavage of the C_1-C_2 σ bond



(26)

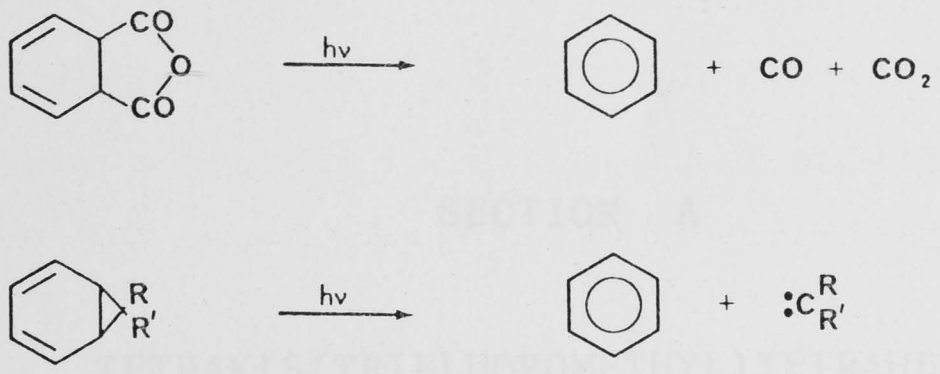
generating a bis-allylic diradical, would be quickly followed

by fragmentation as shown. In cases such as (27) where a bis-allylic diradical would not be formed, fragmentation does not take place[24].



(27)

Other examples of the 1,2-photoaromatization reaction include the photofragmentation of cyclohexadiene anhydrides[25], and the cheletropic cycloelimination of carbenes from norcaradienes[26].



However, these reactions have proved to be of little synthetic importance.

SECTION A

TETRAKIS(TRIFLUOROMETHYL)TETRAHEDRANE —

A PLAUSIBLE SYNTHETIC APPROACH

ABSTRACT

Hexakis(trifluoromethyl)benzvalene, prepared by irradiation of the corresponding benzene, has been shown to react with cyclobutadiene, affording a mixture of *syn* and *anti* 1:1 adducts. Heating these adducts at 240° results in isomerization to 1,2,3,4,5,6-hexakis(trifluoromethyl)tetracyclo[4.4.0.$0^{2,4}$.$0^{3,5}$]deca-7,9-diene, whose behaviour under photolytic and pyrolytic conditions is discussed.

INTRODUCTION

The first serious suggestion that tetrahedranes* might be capable of existence was due to Lipscomb in 1959, who considered the available evidence on the apparent instability of cyclobutadiene, and proposed that a tetrahedral structure might be more stable[27]. Such an isomer would have a closed shell electronic structure, in marked contrast to cyclobutadiene, though the enormous strain energy inherent in such a molecule might nullify this advantage.

Recently, the stability of tetrahedrane with respect to cyclobutadiene, and to two acetylene molecules has been investigated by *ab initio* SCF MO and CI calculations[28]. The simple SCF treatment led to the conclusion that the ground state of tetrahedrane "correlates with a doubly excited state of cyclobutadiene, in which both the lowest and highest π orbitals are doubly occupied". This method thus predicts that ground-state conversion of tetrahedrane to cyclobutadiene would require a substantial activation energy. A similar result was obtained by comparing tetrahedrane with two acetylene molecules†. More sophisticated (CI) calculations predict that cyclobutadiene (in its rectangular ground state) would be

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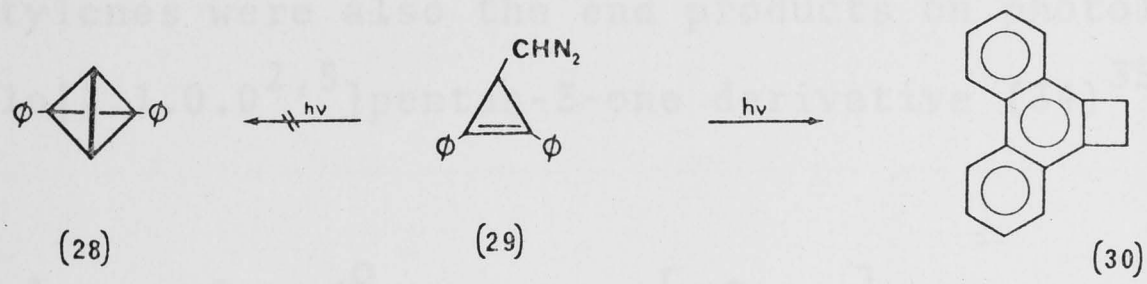
* Tricyclo[1.1.0.$0^{2,4}$]butanes.

† In orbital symmetry terms, the conversion of tetrahedrane to cyclobutadiene is a $-[{}_{\pi}2_{a} + {}_{\pi}2_{a}]$ process, while the cleavage of tetrahedrane to two acetylene molecules may be classified as $-[{}_{\pi}2_{s} + {}_{\pi}2_{s} + {}_{\pi}2_{a} + {}_{\pi}2_{a}]$. Both are symmetry-disallowed in the ground state[9].

70 kcal/mole more stable than tetrahedrane, while dissociation into two molecules of acetylene should be exothermic by 70 to 100 kcal/mole. However, because of the limitations of the calculations, these results must be treated with caution[28].

This "theoretical instability" should not be taken to preclude the existence of this strained molecule. For example, substituted prismane derivatives are unstable with respect to the corresponding benzene by *ca.* 90 kcal/mole[29]. That prismane derivatives exist is simply due to the symmetry-imposed activation energy for conversion to more stable products[9].

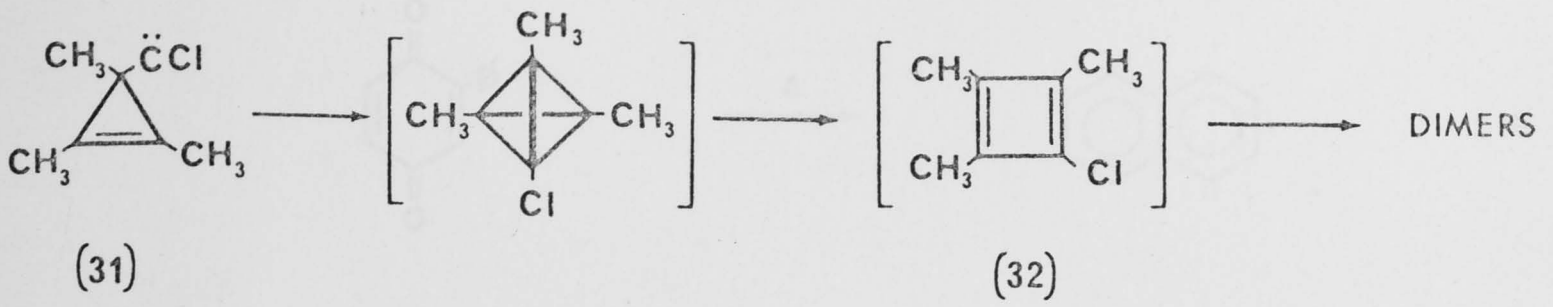
Initial attempts at the synthesis of tetrahedranes have centred on the insertion of carbenes into cyclopropene double bonds. Thus, irradiation of 1,2-diphenylcyclopropenyldiazomethane (29) was thought to have yielded diphenyltetrahedrane (28) in minute yield[30].



(28) (29) (30)

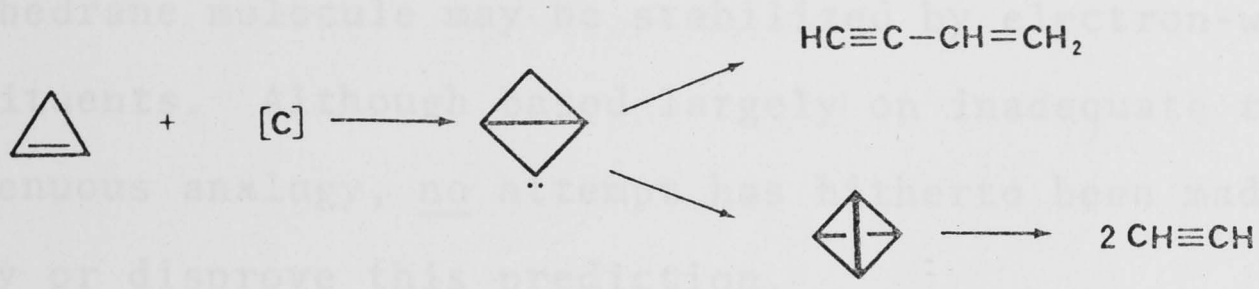
However, the synthesis could not be repeated by other workers[31] [who suggested structure (30) for the product] and the claim was subsequently withdrawn[32].

The intermediacy of a tetrahedrane has been suggested in the rearrangement of the cyclopropenylcarbene (31) to the cyclobutadiene (32)[33], though a single ring-expansion step is entirely feasible.



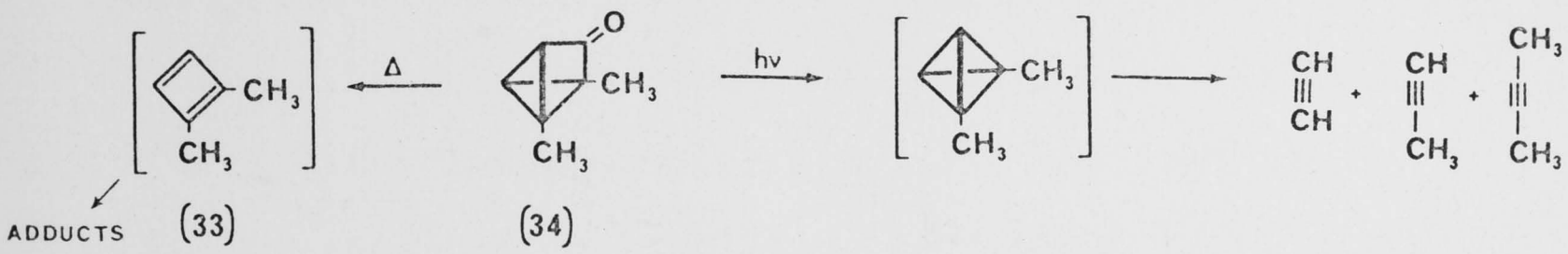
(31) (32)

Reaction of atomic carbon or carbonylcarbene (a carbon atom donor) with cyclopropene gives vinylacetylene and acetylene[34].



The formation of the latter product was interpreted in terms of a tetrahedral intermediate, and further evidence to this effect was obtained by the use of ^{14}C and deuterium labelled precursors.

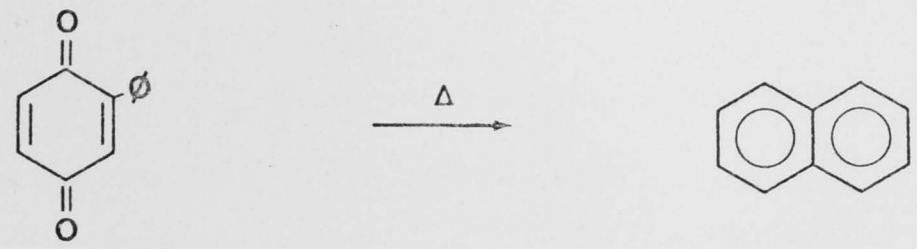
Acetylenes were also the end products on photolysis of the tricyclo[2.1.0.$0^{2,5}$]pentan-3-one derivative (34)[35].



(33) (34)

Again this was interpreted as evidence of a transient tetrahedral species. Under thermolytic conditions, adducts derived from the cyclobutadiene (33) could be obtained.

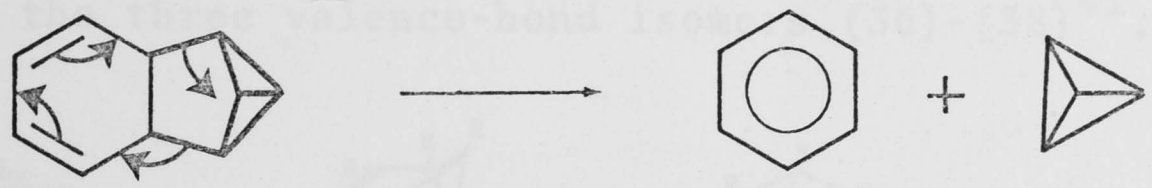
The suggestion that phenyltetrahedrane might be an intermediate in the formation of naphthalene on flash vacuum pyrolysis of phenyl-*p*-benzoquinone[36] may be considered highly speculative.



These experiments indicate that tetrahedranes have little more than transient existence under conditions necessary for their formation. However, it has been suggested[27] that the tetrahedrane molecule may be stabilized by electron-withdrawing substituents. Although based largely on inadequate theory and tenuous analogy, no attempt has hitherto been made to verify or disprove this prediction.

DISCUSSION

In order to apply the 1,2-photoaromatization reaction to the synthesis of a tetrahedrane, a tetracyclo-[4.4.0.$0^{2,4}$.$0^{3,5}$]deca-7,9-diene derivative was required. However, despite much recent interest in $(CH)_{10}$ ring systems[37], such a derivative has not previously been prepared.



As a route to this ring system, it was hoped to utilize a derivative of benzvalene, which incorporates some of the required structural features. Selection of the hexakis(trifluoromethyl) derivative resulted from consideration of several factors:

(1) the bulky electron-withdrawing trifluoromethyl substituents which stabilize the benzvalene should also stabilize the desired tetrahedrane;

(2) these same substituents should increase the reactivity of the benzvalene in cycloadditions to the olefinic centre;

and (3) at the time of commencement of this study, this was the most readily available benzvalene derivative*.

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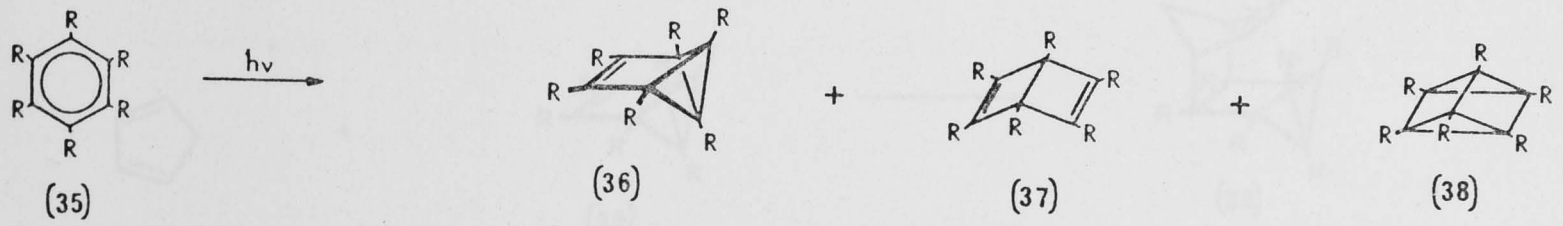
* The parent hydrocarbon is now also readily available, but is much more unstable[38].

Accordingly, hexakis(trifluoromethyl)benzene (35) was prepared by thermal trimerization of hexafluorobut-2-yne under autogenous pressure. A modification of the method of Brown *et. al.*[39] was employed*. The product, a colourless crystalline solid, exhibited only a singlet in the ^{19}F n.m.r. spectrum. The u.v. [λ_{max} 285 nm, ε 140] and mass spectra (molecular ion *m/e* 486) were also consistent with the structural assignment, and clearly showed that the product was neither of the tetramers reported by some previous workers[40].

Irradiation of hexakis(trifluoromethyl)benzene in the vapour phase or in perfluoro-*n*-pentane solution has been shown to yield the three valence-bond isomers (36)-(38)[41].



(35) (36) (37) (38)

The benzvalene (36) was the major product in the early stages, while further irradiation gave increasing amounts of the Dewar benzene (37) and the prismane (38).

Since the benzvalene exhibits no absorption in the u.v. above 230 nm, it was thought that irradiation through a vycor filter (λ>230 nm) might yield this isomer almost exclusively. This expectation was subsequently realized. Irradiation of (35) in acetone solution through a vycor filter for 16 hours resulted in *ca.* 32% conversion to the benzvalene (36) while neither (37) nor (38) was formed. The unreacted benzene was

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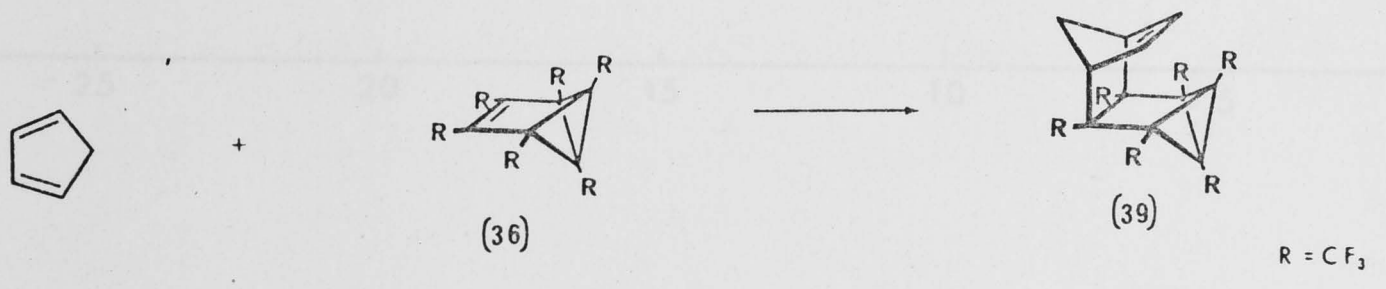
* Considerable difficulty was initially encountered, as the reaction did not proceed in pyrex tubes until the glass was etched. The reaction appears to require surface catalysis.

readily recovered. The benzvalene could thus be obtained in gram quantities, and was shown by its ^{19}F n.m.r. spectrum (see page 16) and other properties to be identical to that previously reported[41].

Hexakis(trifluoromethyl)benzvalene has been shown to react readily with cyclopentadiene, though little evidence was cited to support the structure of the product[42]. Reaction of these compounds was indeed rapid, being complete within a few minutes at room temperature, and afforded a single crystalline product in good yield. Clearly a 1:1 adduct from its analytical data and mass spectrum, structure (39) followed from consideration of its p.m.r. and ^{19}F n.m.r. spectra.



The *endo* stereochemistry of the adduct also followed from the ^{19}F n.m.r. spectrum* (see page 16) in which the trifluoromethyl groups at C_8 and C_9 appear at 24.2 and 20.8 δ - a difference of 3.4 δ. This reflects a marked difference in environment at these two positions, which is more easily attributable to shielding effects in (39) than to steric effects in the alternative isomer†. Exclusive formation of (39) appears to be due to favourable secondary orbital overlap in the transition state for *endo* cycloaddition, and to unfavourable van der Waals repulsion between the methylene

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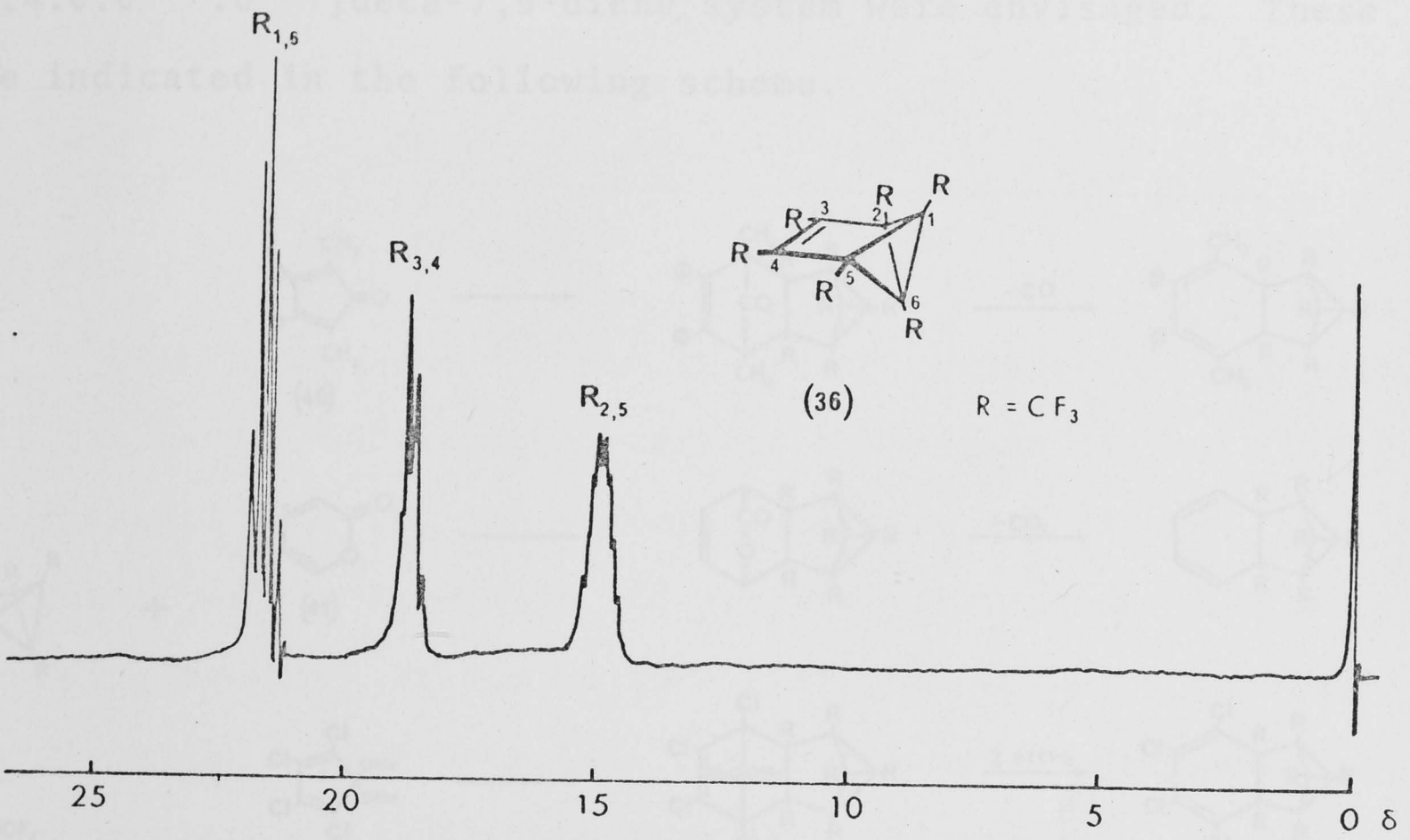
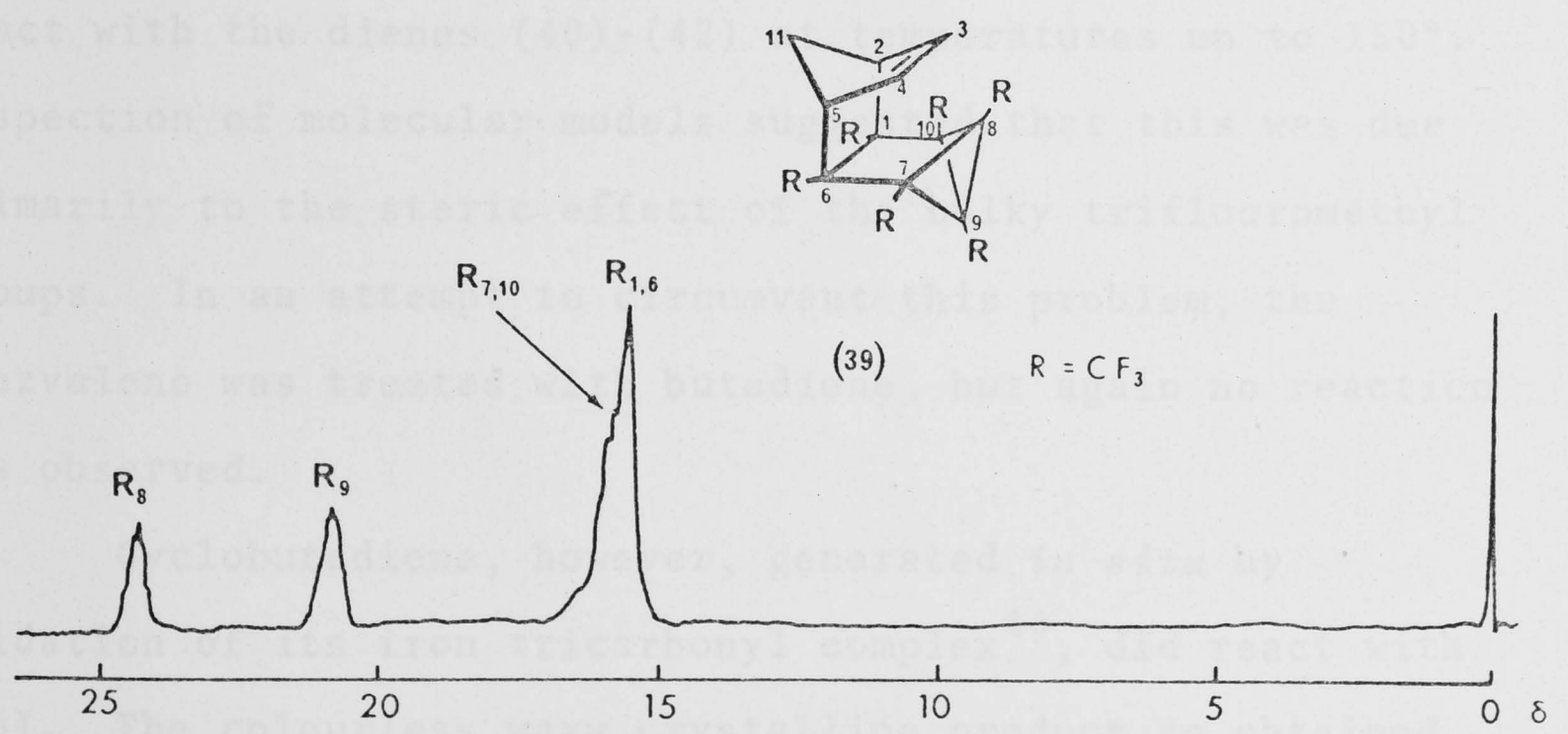
* All ^{19}F n.m.r. chemical shifts are expressed in δ p.p.m. downfield from external trifluoroacetic acid.

† Further discussion of the stereochemistry of benzvalene adducts appears on page 18.

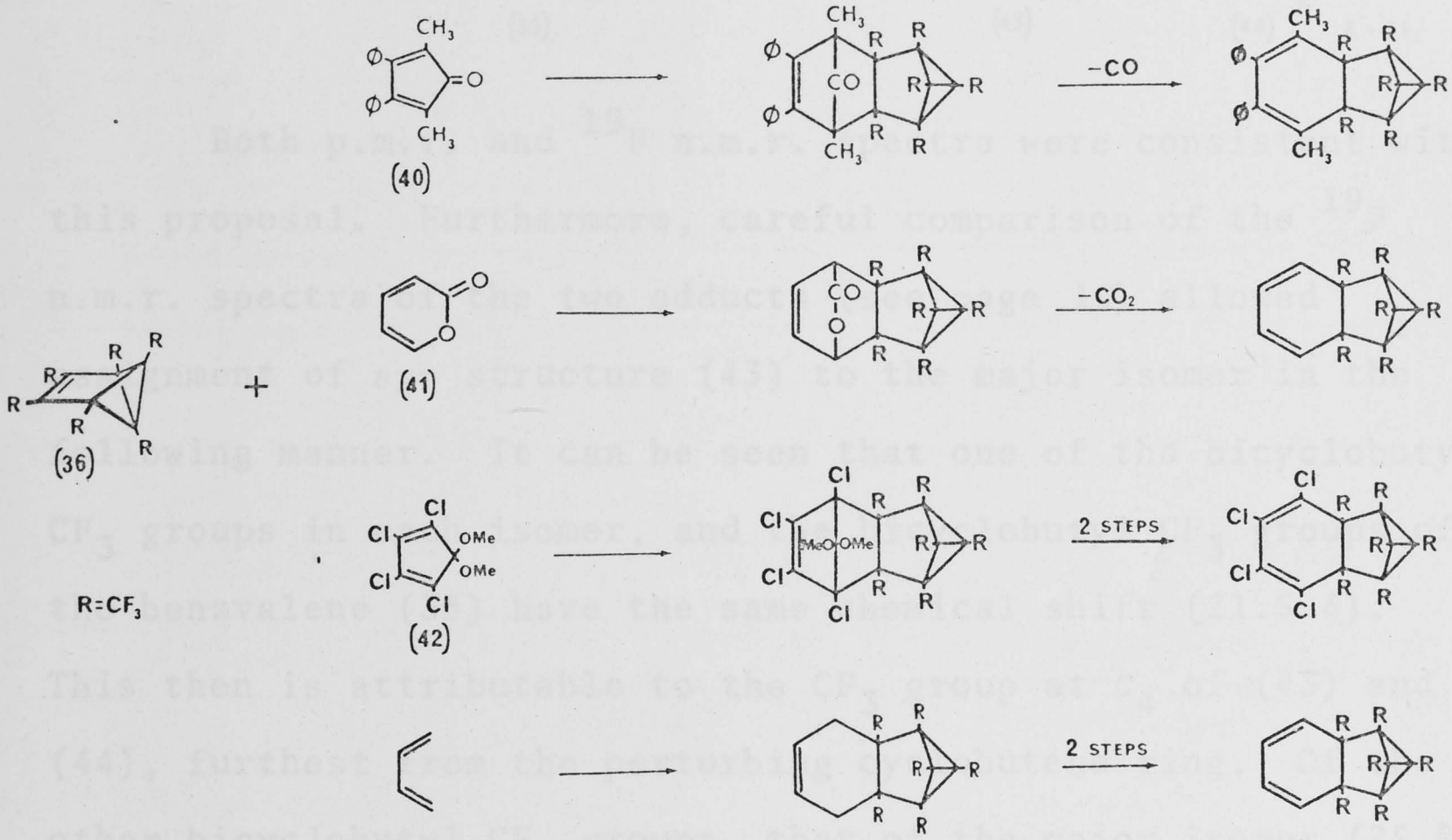




^{19}F n.m.r. spectra of hexakis(trifluoromethyl)benzvalene (36) (neat), and its cyclopentadiene adduct (39) (acetone solution).

protons and the carbon skeleton of (36) in the corresponding *exo* transition state[43].

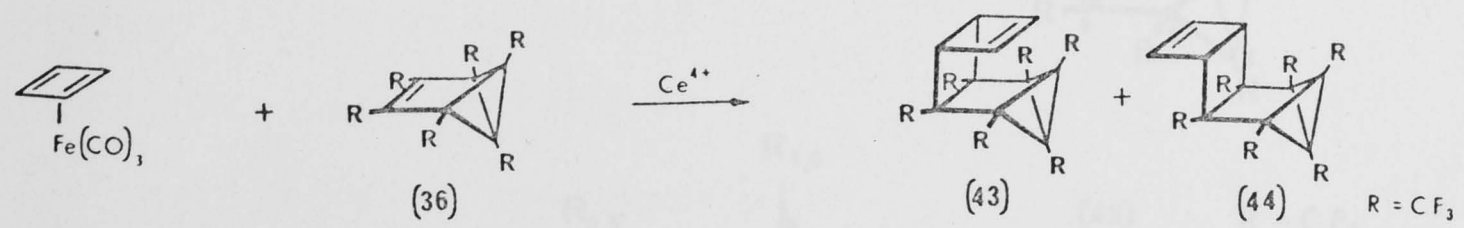
A number of possible routes to the required tetracyclo-[4.4.0.$0^{2,4}$.$0^{3,5}$]deca-7,9-diene system were envisaged. These are indicated in the following scheme.



However, hexakis(trifluoromethyl)benzvalene did not react with the dienes (40)-(42) at temperatures up to 150°. Inspection of molecular models suggested that this was due primarily to the steric effect of the bulky trifluoromethyl groups. In an attempt to circumvent this problem, the benzvalene was treated with butadiene, but again no reaction was observed.

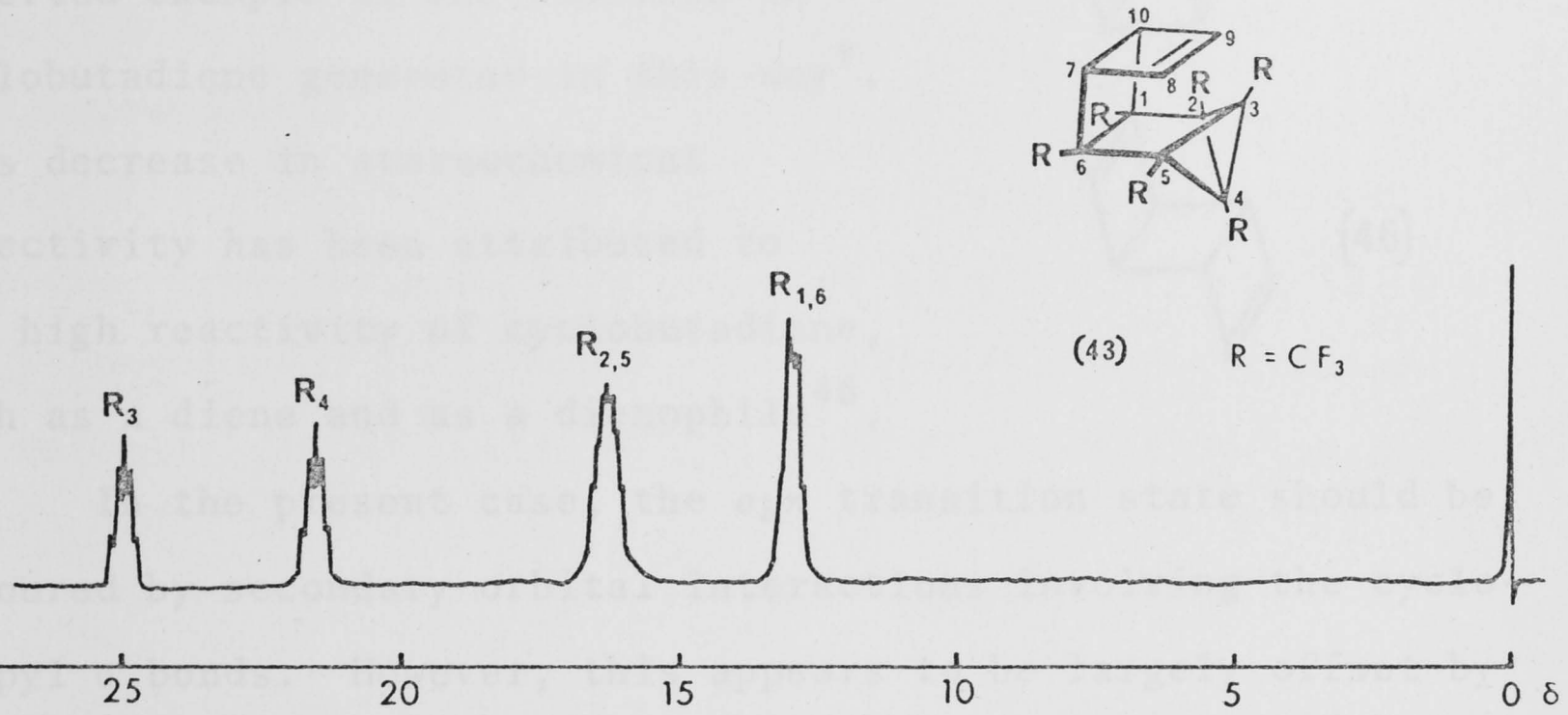
Cyclobutadiene, however, generated *in situ* by oxidation of its iron tricarbonyl complex[44], did react with (36). The colourless waxy crystalline product so obtained was shown by g.l.c. to be a mixture of two compounds (ratio 3:2, 52% yield) and these were separated by preparative scale

g.l.c. That both were 1:1 adducts was clear from the high and low resolution mass spectra, and from analytical data, and the structures (43) and (44) were suggested.

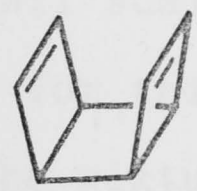


Both p.m.r. and ^{19}F n.m.r. spectra were consistent with this proposal. Furthermore, careful comparison of the ^{19}F n.m.r. spectra of the two adducts (see page 19) allowed assignment of *syn* structure (43) to the major isomer in the following manner. It can be seen that one of the bicyclobutyl CF_3 groups in each isomer, and the bicyclobutyl CF_3 groups of the benzvalene (36) have the same chemical shift (21.5 δ). This then is attributable to the CF_3 group at C_4 of (43) and (44), furthest from the perturbing cyclobutene ring. Of the other bicyclobutyl CF_3 groups, that of the major isomer (25.0 δ) is at much lower field than the other (23.5 δ). Inspection of molecular models shows that the CF_3 group at C_3 of (43) lies within the *deshielding* zone of the cyclobutenyl double bond, and should thus appear at lower field than that of (44). Again, the CF_3 groups at C_1 and C_6 of (44) lie within the *shielding* zone of the cyclobutenyl double bond, and should thus appear at higher field (9.4 δ) than the corresponding CF_3 groups of (43) (12.9 δ).

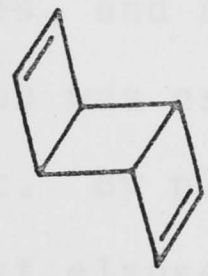
Predominance of the *syn* isomer might be expected on the basis of Diels-Alder rules[45], but the proportion of the *anti* isomer (40%) is much higher than previously observed in (4 + 2)π cycloadditions of cyclobutadiene[44]. Indeed, formation of the


10
9
7
8
1
2
3
R
R
R
R
R
R
6
5
4
R
R
R
R
R
R

syn (45) and *anti* (46) cyclobutadiene dimers[46] (ratio* 5:1) is the *only* reported example of *exo* addition to cyclobutadiene generated in this way†. This decrease in stereochemical selectivity has been attributed to the high reactivity of cyclobutadiene, both as a diene and as a dienophile[46].



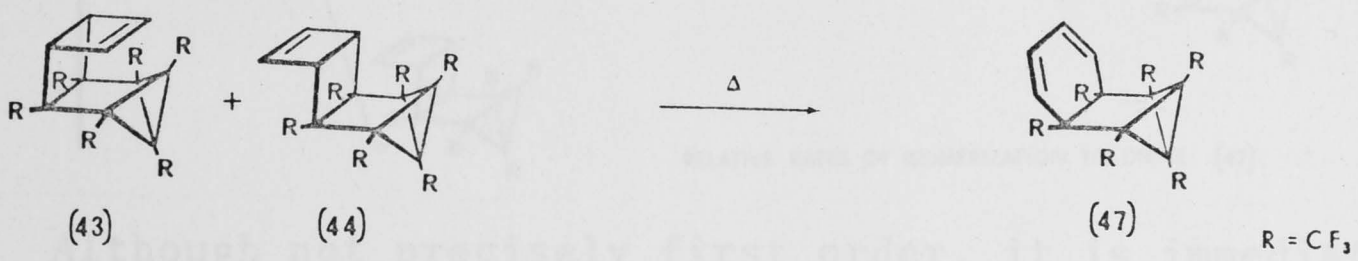
(45)



(46)

In the present case, the *syn* transition state should be favoured by secondary orbital interactions involving the cyclopropyl σ bonds. However, this appears to be largely offset by van der Waals repulsive forces, probably involving the trifluoromethyl groups[43].

It was hoped that the pentacyclic derivatives (43) and (44) could be thermally isomerized to the tetracyclo-[4.4.0.$0^{2,4}$.$0^{3,5}$]deca-7,9-diene derivative (47), the required tetrahedrane precursor.



(43) (44) (47) R = CF_3

This proved to be the case. Although quite stable below 200°, heating at 240° caused slow conversion of (43) and (44) to a single product having a substantially longer g.l.c. retention

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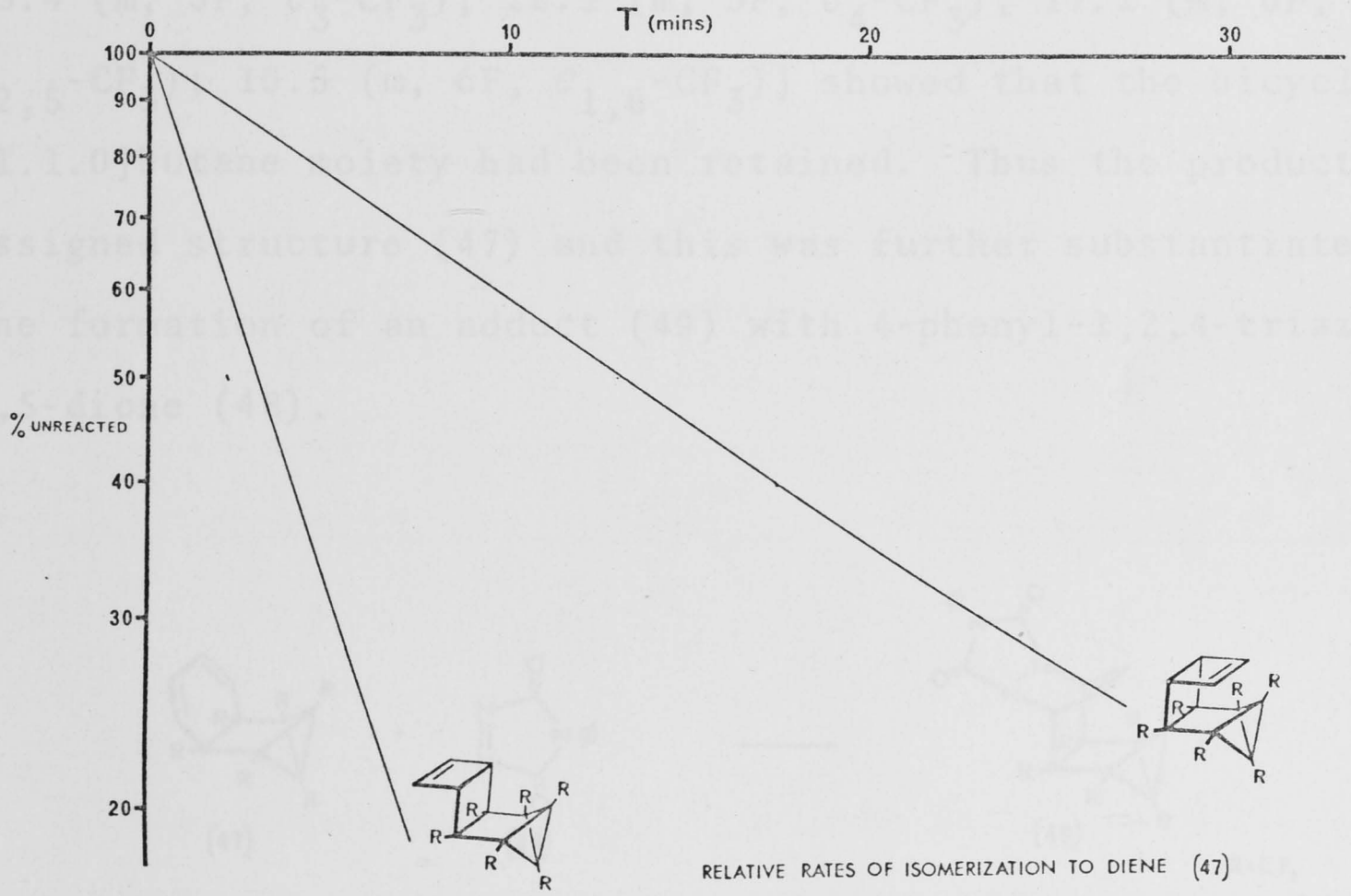
* The ratio of (45) to (46) formed on dimerization of cyclobutadiene under these conditions is solvent dependent[47]. The ratio varies from 2:1 (in acetic acid) to 100:1 (in dimethylformamide).

† Formation of the *syn* isomer on dimerization of cyclobutadiene generated by other methods has been attributed to intermediate organo-metallic species[48].

time. Initial experiments, conducted on a small scale, were designed to determine optimum conditions for this conversion*. Accordingly, small samples of the mixture of cyclobutenes were sealed into small glass tubes, and heated at 240° for periods up to 1 hour, when reaction was essentially complete. The products were analyzed by g.l.c. By plotting the proportion of each isomer remaining against elapsed time, the rates of isomerization of (43) and (44) could be compared.



RELATIVE RATES OF ISOMERIZATION TO DIENE (47)

Although not precisely first order, it is immediately apparent that isomerization of the *anti* isomer (44) is approximately four times more rapid than that of (43). This may be interpreted as indicating some degree of *bonding interaction* between the cyclobutenyl double bond and the cyclopropyl σ bonds in (43). [In the absence of such an

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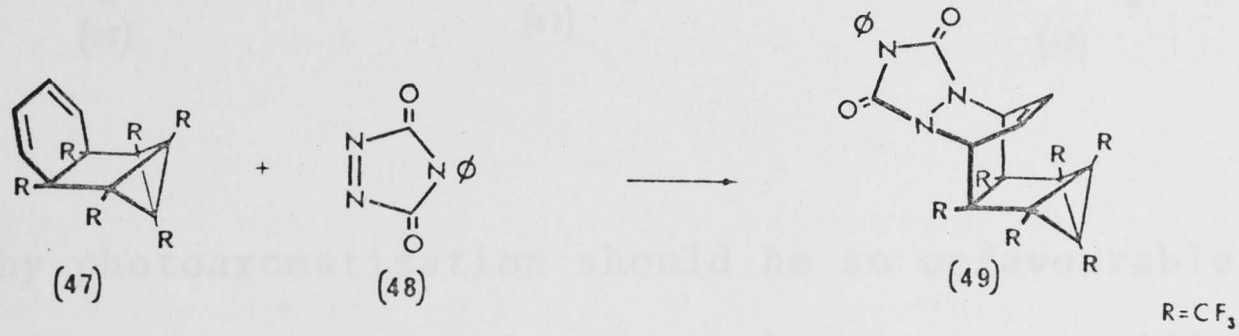
* Heating at 260° caused more rapid reaction, but gave in addition to (47) another product showing a broad u.v. absorption at 275.5 nm. This product could not be identified.

effect, steric repulsion in (43) should make this isomer isomerize *more* readily than (44)].

The product, a colourless crystalline solid, was shown to be isomeric with the starting cyclobutenes by analysis and by its mass spectrum (*vide infra*). Its u.v. spectrum [λ_{max} (EtOH) 251, 258, 268 nm, ε 4350, 4400, 2500] and p.m.r. spectrum [$CDCl_3$, δ p.p.m. : 6.6-6.3 (m, 2H, $C_{8,9}$-H); 6.3-5.9 (m, 2H, $C_{7,10}$-H)] suggested that a cyclohexadiene ring was present, while its ^{19}F n.m.r. spectrum [$CHCl_3$, δ p.p.m. : 23.4 (m, 3F, C_3-CF_3); 22.1 (m, 3F, C_4-CF_3); 17.1 (m, 6F, $C_{2,5}$-CF_3); 10.5 (m, 6F, $C_{1,6}$-CF_3)] showed that the bicyclo-[1.1.0]butane moiety had been retained. Thus the product was assigned structure (47) and this was further substantiated by the formation of an adduct (49) with 4-phenyl-1,2,4-triazoline-3,5-dione (48).

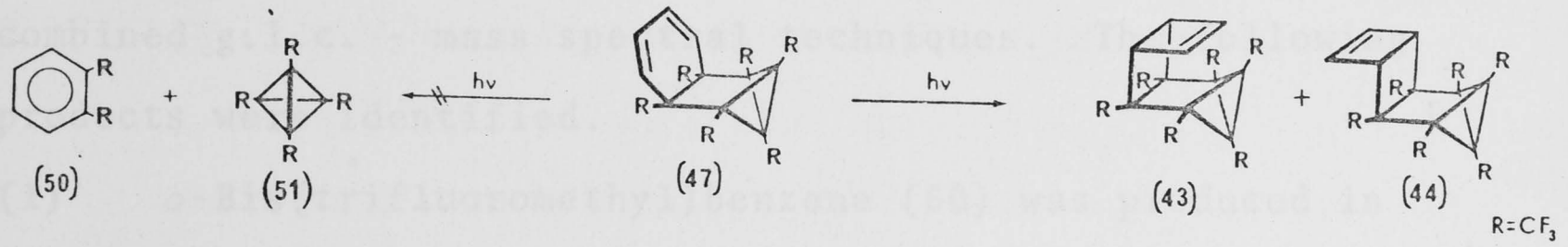


The extreme slowness of this reaction (only 72% completion after 24 hours at room temperature) indicated that both sides of the diene (47) are sterically hindered. Thus two structures are possible for the adduct, depending on the direction of approach of the dienophile. The structure depicted above is considered more likely, however, because of the marked similarity between the ^{19}F n.m.r. spectrum of this product and that of the benzvalene-cyclopentadiene adduct (39).

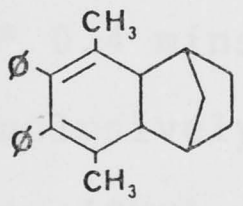
The mass spectrum of (47) showed, besides successive losses of F and CF_3 from the molecular ion (*m/e* 538), peaks

at *m/e* 214 (54%) and 324 (59%). The former corresponds to *o*-bis(trifluoromethyl)benzene (50), while the latter is presumably a $C_4(CF_3)_4$ fragment. Although mass spectral fragmentation patterns are not necessarily followed in the corresponding thermal or photochemical processes[49], it was hoped that this might be so in the present case.

Irradiation (λ>230 nm) of the diene (47) in ether was performed at 0°, and monitored by g.l.c. Instead of photoaromatization however [(50) was not detected], intramolecular cyclization occurred, affording in high (87%) yield the original cyclobutenes (43) and (44). A minor photoproduct (13%) was not identified, but was thought to be isomeric with (47) because of its comparable g.l.c. retention time.



Why photoaromatization should be so unfavourable in this system is not completely clear, but it is significant that in all cases so far studied [e.g. (27)] in which 1,2-photoaromatization would require formation of a new σ bond, this reaction is not observed[24].



(27)

Attention was then turned to pyrolysis of the diene (47). Although recovered unchanged after brief heating in a sealed tube at 340°, fragmentation did occur under flash vacuum pyrolysis conditions.

The apparatus used was of quite simple design, being intended only for initial experiments. A 10 x 2½ cm quartz tube packed with quartz chips and enclosed in a horizontal tube furnace, was fitted at one end with a flask containing the starting material, while the other end led through a cold-trap to a conventional vacuum system. The trap was fitted with two taps to permit sealing and disconnection from the vacuum line.

The flask containing the starting diene (47) was cooled in liquid nitrogen until a satisfactory vacuum (0.001 mm) was established, and then warmed to 50°, to allow slow sublimation of the contents through the pyrolysis tube, which was pre-heated to 700°. 2 mg to 250 mg quantities were successfully handled in this way. The pyrolysis products were analyzed by p.m.r., ^{19}F n.m.r. and mass spectrometry, and by g.l.c. and combined g.l.c. - mass spectral techniques. The following products were identified.

(1) *o*-Bis(trifluoromethyl)benzene (50) was produced in high yield, and was identified by g.l.c. (retention time* 6.8 mins) and spectral comparison with an authentic sample prepared from hexafluorobut-2-yne and cyclohexadiene (with thermal elimination of ethylene from the initially formed adduct).

(2) Hexafluorobut-2-yne (retention time* 0.4 mins) was produced in lower yield, and was conclusively identified by its ^{19}F n.m.r. spectrum [$CHCl_3$, 24.1 δ (s)] and mass spectrum [*m/e* 162 (molecular ion, 31%), 143 (55%), 93 (64%), 69 (base peak)], and by the formation of a 1:1 adduct (52) with

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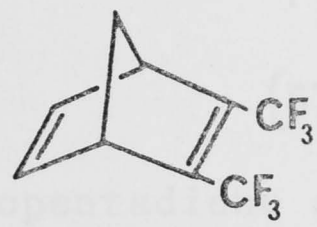
* Retention times quoted refer to a 3' x 1/8" column of 5% SE30 on Varaport 30 at 0°.

cyclopentadiene, which was compared with authentic material.

(3) A volatile product (53) (retention time* 0.8 mins), whose mass spectrum (molecular ion *m/e* 462) suggested the molecular formula $C_4(CF_3)_6$, was formed in variable, though usually small amounts.

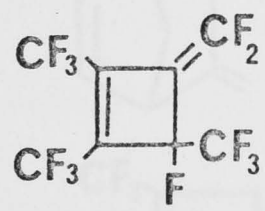


(52)

(4) A less volatile product (54) (retention time* 2.4 mins) was assigned the molecular formula $C_8(CF_3)_8$ on the basis of its mass spectrum (molecular ion *m/e* 648). This product too was formed in variable, but usually small amounts.

(5) The major volatile product however (retention time* 0.7 mins) had the molecular formula $C_4(CF_3)_4$ (molecular ion *m/e* 324). Subsequent interest centred on this product.

The simplicity of the ^{19}F n.m.r. spectrum [$CDCl_3$, 25.3 δ (s)] indicated a high degree of symmetry, and immediately eliminated from consideration all structures [e.g. (55)] resulting from intramolecular fluorine shift. Only the tetrahedrane (51), the cyclobutadiene (56) and the butatriene (57) were consistent with the spectral data.



(55)

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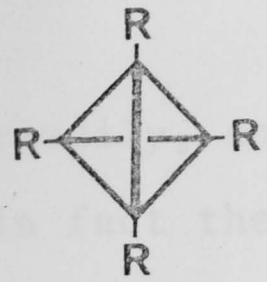
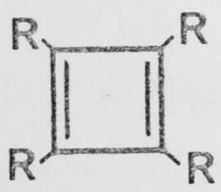
* See footnote previous page.



(51)

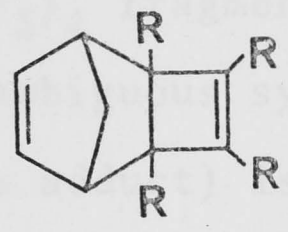


(56)

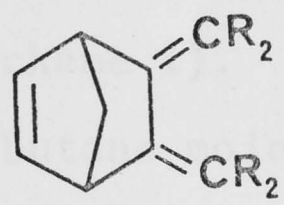
$R_2C{=}C{=}C{=}CR_2$

(57) $R = CF_3$

Reaction with an excess of cyclopentadiene at room temperature produced a 1:1 adduct [molecular ion *m/e* 390; p.m.r. ($CDCl_3$, δ p.p.m.): 6.96 (t, 2H, olefinic protons); 3.80 (m, 2H, bridgehead protons); 2.40 (m, 2H, methylene protons); ^{19}F n.m.r. ($CHCl_3$, δ p.p.m.): 13.5 (m, 6F); 13.1 (m, 6F)]. These spectra were in accord with structure (58), the anticipated cyclobutadiene adduct, and with (59), which might arise from addition to the butatriene[50]. However, the u.v. spectrum of the adduct [λ_{max} (EtOH) 234, 279 (infl.) nm, ε *ca.* 2000, 700]*, and certain features of the i.r. spectrum, for example the weak bands at 1640 and 1678 cm^{-1},† were more consistent with the diene structure (59). Again, the cyclobutadiene (56) would be expected to dimerize



(58)



(59) $R = CF_3$

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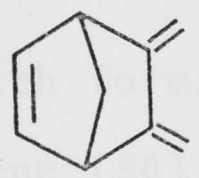
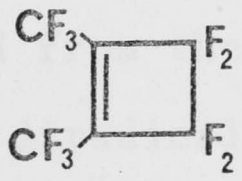
* The u.v. spectrum of the parent compound (60) shows λ_{max} 241 nm, ε 9400[51].

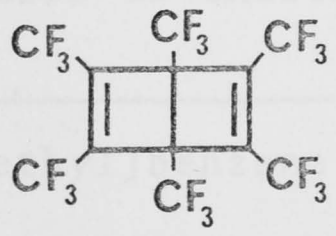
† The C=C stretching absorption of (61) appears at 1715 cm^{-1},[52] while that of the Dewar benzene (37) has been reported at 1701 and 1709 cm^{-1}.[41]



(60)



(61)



(37)

readily, and to form a 1:2 adduct with cyclopentadiene, when in fact the $C_4(CF_3)_4$ product was quite stable at room temperature, and no trace of a 1:2 adduct (molecular ion *m/e* 456) was found. Formation of a cyclopentadiene adduct by the tetrahedrane (51) was not considered likely, on account of the known stereochemical requirements of additions to bicyclo[1.1.0]butane systems[53]. In any case, no adduct derivable from the tetrahedrane could be consistent with the observed spectral data.

Thus all the data appear consistent with assignment of the butatriene structure (57) to the $C_4(CF_3)_4$ fragment, but this cannot be considered proven until unambiguous synthesis of this product (or of its cyclopentadiene adduct) is achieved.

It is interesting to speculate on the mechanism of formation of the pyrolysis products (see Scheme 1).

Rearrangement of the bicyclo[1.1.0]butane moiety in (47) prior to aromatization [e.g.to the *cis*-dihydronaphthalene (62)] is ruled out by the complete absence in the pyrolysate of hexakis(trifluoromethyl)benzene (35). Two modes of fragmentation of the diene are likely*:

(1) non-concerted cleavage of the 1,2 σ bonds producing *o*-bis(trifluoromethyl)benzene (50) and the bicyclo-[1.1.0]butane diradical (63),

or (2) a concerted electrocyclic reaction with formation of the benzene (50) and the cyclobutadiene (56).

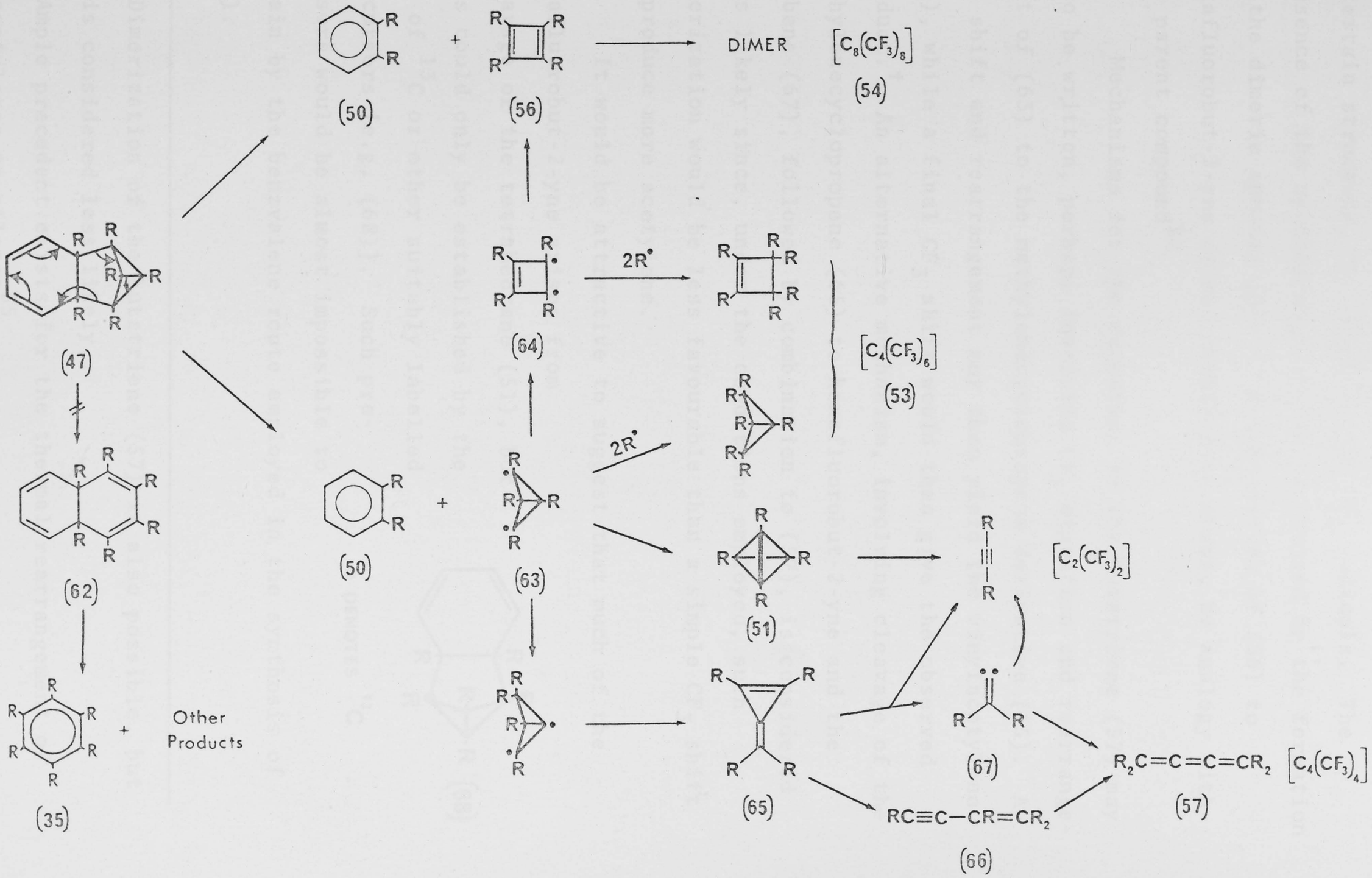
The cyclobutadiene may also be formed from the diradical (63), perhaps *via* the cyclobutene diradical (64). The presence of intermediate diradical species is indicated

---

* Concerted formation of *o*-bis(trifluoromethyl)benzene (50) and the tetrahedrane (51) is improbable.

SCHEME 1

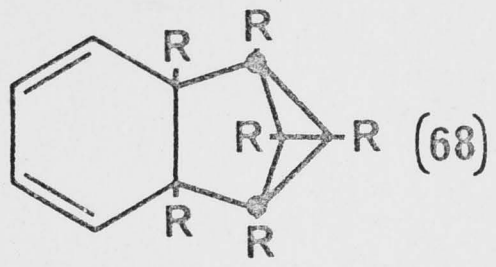
Pyrolytic Fragmentation of the Diene (47) (R=CF_3)



by the observed formation of $C_4(CF_3)_6$ products (53), of uncertain structure, by trapping with CF_3 radicals. The presence of the cyclobutadiene (56) is implied by the formation of the dimeric species (54).* Fragmentation of (56) to hexafluorobut-2-yne is not expected to occur, by analogy with the parent compound[54].

Mechanisms for the formation of the butatriene (57) may also be written, perhaps involving CF_3 migration and rearrangement of (63) to the methylenecyclopropene derivative (65). A CF_3 shift and rearrangement may then yield the vinylacetylene (66), while a final CF_3 shift would then give the observed product.† An alternative mechanism, involving cleavage of the methylenecyclopropene (65) to hexafluorobut-2-yne and the carbene (67), followed by combination to (57), is considered less likely since, under the conditions employed, such dimerization would be less favourable than a simple CF_3 shift to produce more acetylene.

It would be attractive to suggest that much of the hexafluorobut-2-yne arises from cleavage of the tetrahedrane (51), but this could only be established by the use of ^{13}C or other suitably labelled precursors [e.g. (68)]. Such precursors would be almost impossible to obtain by the benzvalene route employed in the synthesis of (47).



(68)

● DENOTES ^{13}C

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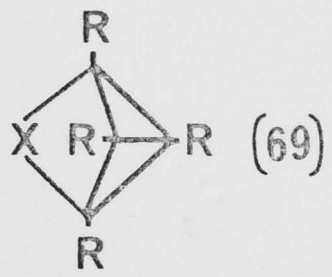
* Dimerization of the butatriene (57) is also possible, but is considered less likely.

† Ample precedent exists for the thermal rearrangement of acetylenes to allenes[55].

In conclusion, it appears that the 1,2-aromatization reaction, either photochemical or thermal, is unsuited to the preparation of strained σ systems such as tetrahedranes. Synthetic attempts involving low-temperature photochemical elimination of small neutral molecules X (e.g. CO^{35}, CO_2, N_2, etc.) from compounds of type (69) appear to be more promising.



(69)

SECTION B

1,2-DIAZET-3-INE —

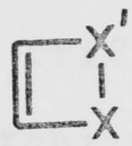
A NOVEL 6π-ELECTRON FOUR-MEMBERED HETEROCYCLE

ABSTRACT

The 1,2-photoaromatization reaction has been applied to the synthesis of 1,2-dimethoxycarbonyl-1,2-diazet-3-ine, a novel heterocycle for which naive application of the Hückel $(4n + 2)\pi$ rule would predict aromatic character. Simple HMO calculations are performed, and the properties and structure of the ring system discussed.

INTRODUCTION

1,2-Diazet-3-ine is a member of a class of four-membered heterocycles (70) which satisfy the Hückel $(4n + 2)\pi$ criterion for aromatic character.

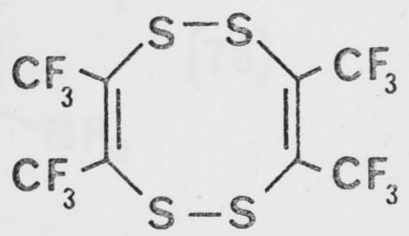


(70)

X, X' = O, S, NR, etc.

Very few molecules possessing these structural features have been investigated, though a number of derivatives (e.g., with X = O, X' = SR_2 or X = NR, X' = PR_3) have been suggested as intermediates in the addition of acetylenes to hetero-olefins[56]. Indeed, the only heterocycle of this type which has been isolated and characterized is the 1,2-dithiete (71)[57]. Prepared by reaction of hexafluorobut-2-yne with elementary sulphur, this product exhibited considerable thermal stability. Thus, although slow dimerization to (73) occurred at room temperature, (71) could be recovered from the dimer by pyrolysis. The corresponding dicyano derivative (72) was trapped as adducts with electron-rich olefins, but could not be isolated[58].

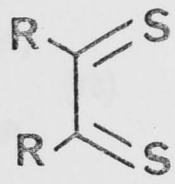
(71) R = CF_3
(72) R = CN



(73)

Simmons *et al.* have examined the effect of substituents at the C_2 and C_3 positions of the dithiete ring[58]. LCAO-MO calculations showed that electron-withdrawing substituents

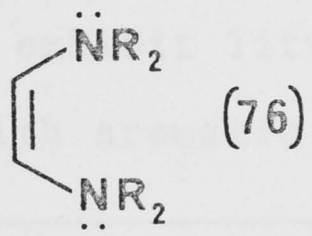
such as CF_3 or CN had the effect of increasing the sulphur-sulphur bond order, thus stabilizing the ring structure [with respect to the α-dithioketone isomer


(74)

(74)], while electron-donating substituents such as NMe_2 had the reverse effect*. The observed stability of the dithiete (71) may thus be partly due to the electron-withdrawing trifluoromethyl substituents, while at least some additional stabilization should result from p_π-d_π interaction involving the sulphur *d*-orbitals.

In the diazetine system (75), however, no such additional stabilization is possible, and contradictory predictions have been made regarding its potential aromaticity. It has been stated that the ring has insufficient bonding molecular orbitals for its 6π electrons, and hence could not be aromatic[59]. Simple HMO calculations, however, have suggested that the molecule should possess a low delocalization energy, though this was not estimated[60]. An estimate can be made by applying the simple HMO method (without overlap) to the diazetine (75) and to its isoelectronic open-chain analogue (76)[61].

(75)


(76)

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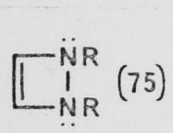
* For similar reasons, it may be anticipated that the diazetine ring would be stabilized by electron-donating substituents on nitrogen. However, no such calculations have been made on this system.

Taking all exchange integrals equal to β and the coulomb integrals $\alpha_C = \alpha$ and $\alpha_N = \alpha + \beta$, the orbital energy levels were calculated and are shown schematically below.



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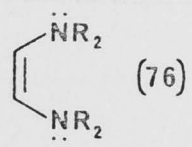

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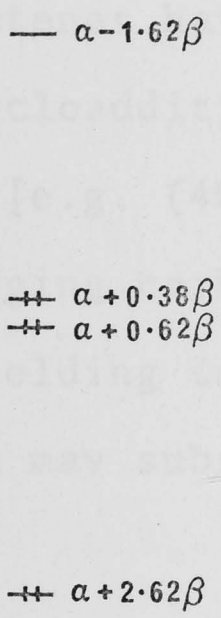

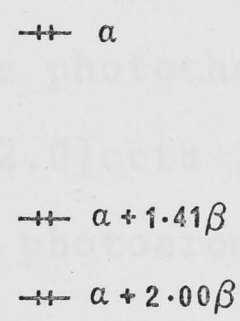

Using these figures, the total π-electron energy of (75) was calculated as $(6\alpha + 7.24\beta)$[60], while that of (76) was $(6\alpha + 6.83\beta)$. The difference (0.41β) represents the additional stabilization energy of the ring structure - a quantity directly related to aromatic resonance energy*.

This rather low value of stabilization energy would be substantially offset by ring-strain in the four-membered ring. 1,2-Diazet-3-ines would thus be expected to exhibit little, if any, of the stability normally associated with aromatic molecules.

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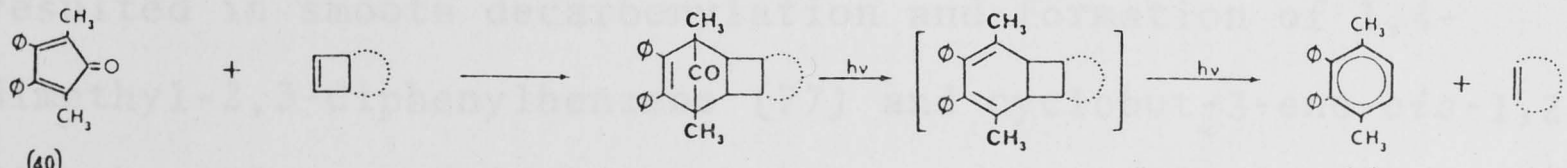
* Although numerous and often conflicting definitions of aromaticity have been suggested[60], that due to Dewar is probably the most useful and is used here[62]. According to this definition, a compound may be considered aromatic if the ground state of the molecule possesses significant delocalization energy relative to selected open-chain analogues.

DISCUSSION

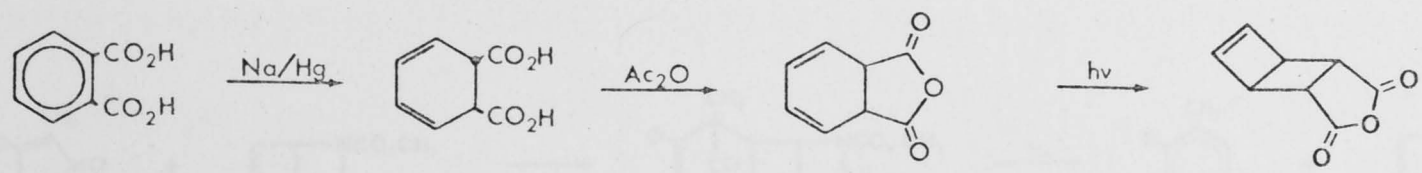
Cyclobutenes have been shown to be effective dienophiles in (4 + 2)π cycloaddition reactions[63]. Addition to cyclopentadienones [e.g. (40)] has been shown to yield adducts from which the bridging carbonyl group may be photochemically eliminated, yielding *in situ* bicyclo[4.2.0]octa-2,4-diene systems, which may subsequently undergo photoaromatization[1].



(40) (77)

By an analogous sequence, it was conceivable that reaction with bicyclo[2.2.0]hex-2-ene systems might yield otherwise inaccessible cyclobutene derivatives.

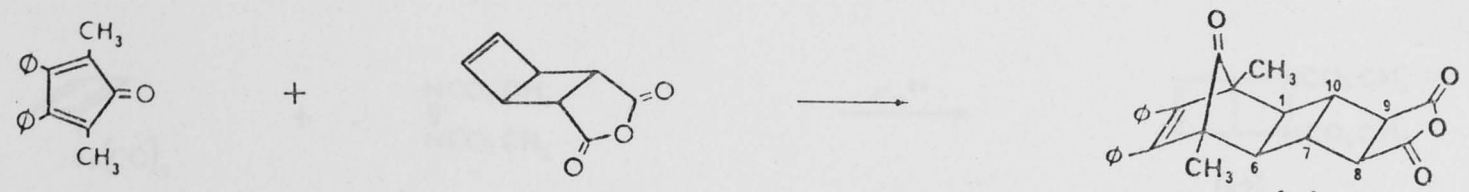
To test this hypothesis, *anti*-bicyclo[2.2.0]hex-5-ene-*cis*-2,3-dicarboxylic anhydride (78) was synthesized from phthalic acid by established procedures[64], and allowed to react with 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone (40) (generated *in situ* from its dimer in refluxing benzene).



(78)

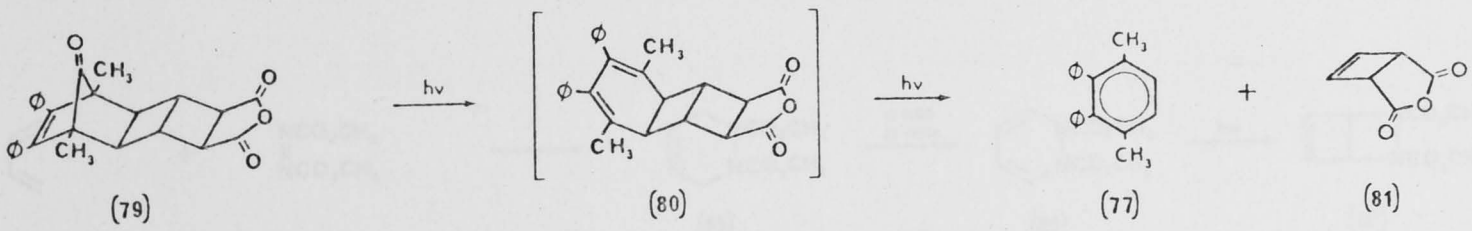
The cycloaddition showed a high degree of stereospecificity, forming two adducts (ratio 9:1, 74% yield).

The major adduct (79) was thought to have the stereochemistry depicted below, resulting from *exo* addition of the dienone onto the least hindered side of the cyclobutene. This *anti*, *anti* stereochemistry about the two cyclobutane rings was supported by the observed lack of coupling between the $C_{1,6}$ (2.84 δ), $C_{7,10}$ (2.76 δ) and $C_{8,9}$ (3.55 δ) cyclobutyl protons in the p.m.r. spectrum[65]. This is consistent with earlier observations of stereoselectivity in related cycloadditions[63].



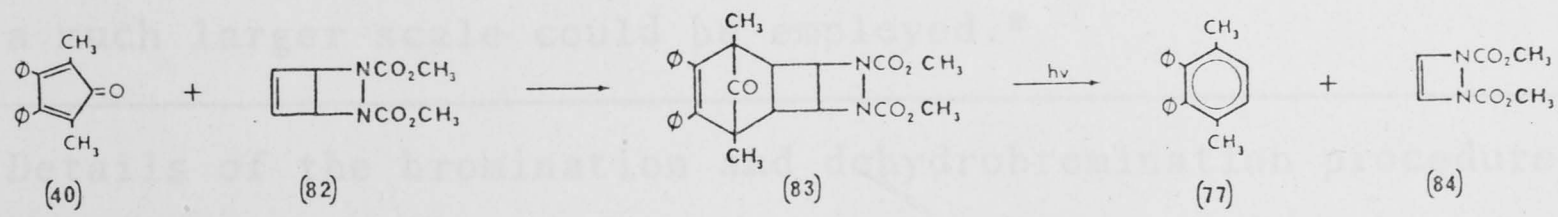
(40) (78) (79)

Irradiation (λ>230 nm) of the bridge-ketone adduct (79) resulted in smooth decarbonylation and formation of 1,4-dimethyl-2,3-diphenylbenzene (77) and cyclobut-3-ene-*cis*-1,2-dicarboxylic anhydride (81), the expected photoaromatization products. The diene (80)was the presumed intermediate, but its presence was not detected.



(79) (80) (77) (81)

The successful preparation of the cyclobutene (81), a known compound in this case, suggested that a similar sequence of reactions might convert the 2,3-diazabicyclo[2.2.0]hex-5-ene derivative (82) to the 1,2-diazet-3-ine (84).



(40) (82) (83) (77) (84)

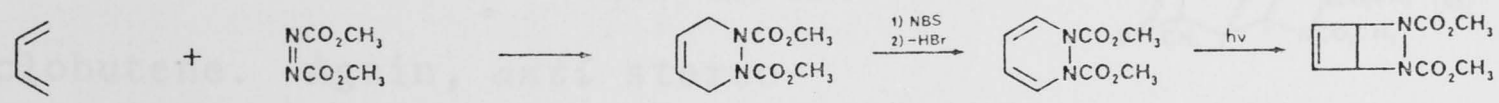
The success or failure of this scheme hinged largely on

the availability of the starting diazabicyclohexene (82). Two possible syntheses of this compound were envisaged.

Addition of cyclobutadiene (generated *in situ* by oxidation of cyclobutadieneiron tricarbonyl with ceric ammonium nitrate) to dimethyl azodicarboxylate, was found to give the product in rather poor yields (*ca.* 30%). This could not be improved by performing the oxidation under nitrogen, or by slight variations in the addition procedure.

(82)

The second synthesis, again starting with dimethyl azodicarboxylate, involved cycloaddition to butadiene[66], followed by allylic bromination with *N*-bromosuccinimide and dehydrobromination to the dihydropyridazine (86)[67]. Irradiation of this diene has been stated to give (82) in good (*ca.* 60%) yield[67].



(85) (86) (82)

Yields obtained in the last step were quite poor (*ca.* 20%), even though care was taken to exclude oxygen from the irradiation vessel. This method still had a slight advantage over that previously mentioned, however, as a much larger scale could be employed.*

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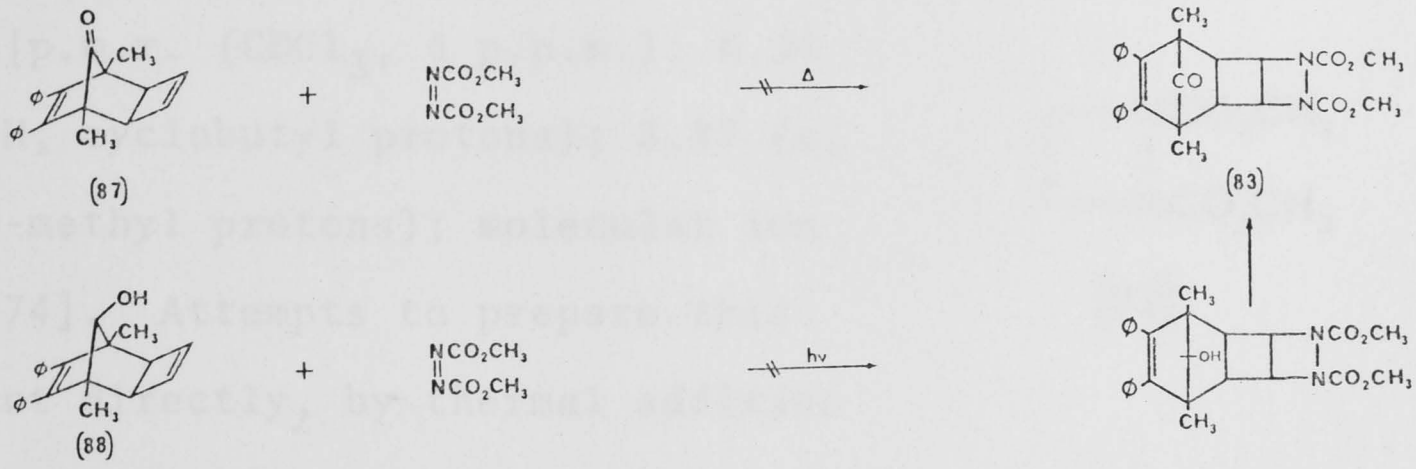
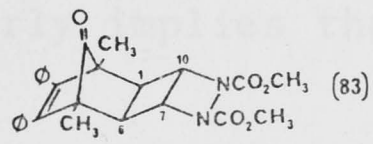
* Details of the bromination and dehydrobromination procedures were kindly supplied by Prof. L.J. Altman of Stanford University, California.

Attempts to prepare the ketone (83) by thermal addition of dimethyl azodicarboxylate to the cyclobutene (87) or by photochemical addition to the cyclobutene (88) were unsuccessful.



Reaction of 2,3-diazabicyclo[2.2.0]hex-5-ene (82) with 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone (40) in refluxing benzene gave the expected adduct (83). The cyclo-addition was again highly stereoselective, forming one isomer almost exclusively, which was thought to have the *exo*, *anti* stereochemistry depicted, resulting from addition of the diene onto the least hindered side of the cyclobutene. Again, *anti* stereo-chemistry about the cyclobutane ring was supported by the lack of coupling between protons at $C_{1,6}$ (3.15 δ) and $C_{7,10}$ (4.46 δ) in the p.m.r. spectrum[65].

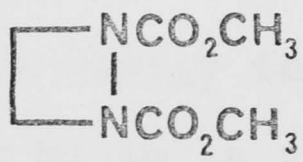


(83)

Irradiation (λ>230 nm) of the adduct was performed at 0°, and carefully monitored by p.m.r. spectroscopy. In addition to 1,4-dimethyl-2,3-diphenylbenzene (77), a quite unstable product was formed, which could be obtained in *ca.* 95% purity by preparative scale t.l.c. The p.m.r. spectrum of this product [$CDCl_3$, δ p.p.m.: 6.57 (s, 2H, olefinic protons); 3.88 (s, 6H, *O*-methyl protons)] was clearly con-

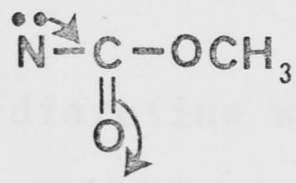
sistent with the diazetine structure, as was the mass spectrum (*m/e* 172).*

More compelling evidence for this assignment was derived from catalytic hydrogenation of the photoproduct, which gave, after absorption of one equivalent of hydrogen, the diazetidine (89) [p.m.r. ($CDCl_3$, δ p.p.m.): 4.34 (s, 4H, cyclobutyl protons); 3.87 (s, 6H, *O*-methyl protons); molecular ion *m/e* 174]. Attempts to prepare this product directly, by thermal addition of ethylene and dimethyl azodicarboxylate did not yield the expected 1:1 adduct[68].



(89)

Comparison of the i.r. spectra† of the diazetine and the derived diazetidine led to some insight into the structure of these products. Thus, the ester carbonyl absorption bands in the diazetine appeared at 1743 and 1776 cm^{-1}, while in the diazetidine, the bands appeared at 1722 and 1759 cm^{-1}, the difference (19 cm^{-1}) indicating substantially more single bond C-O character in the latter case. This clearly implies that resonance contributions of the type illustrated are not operative in the diazetine, which may be interpreted as evidence of *lone pair delocalization* in this molecule.



The presence of two carbonyl absorptions in each case may be due to coupled vibration of the two ester groups, or

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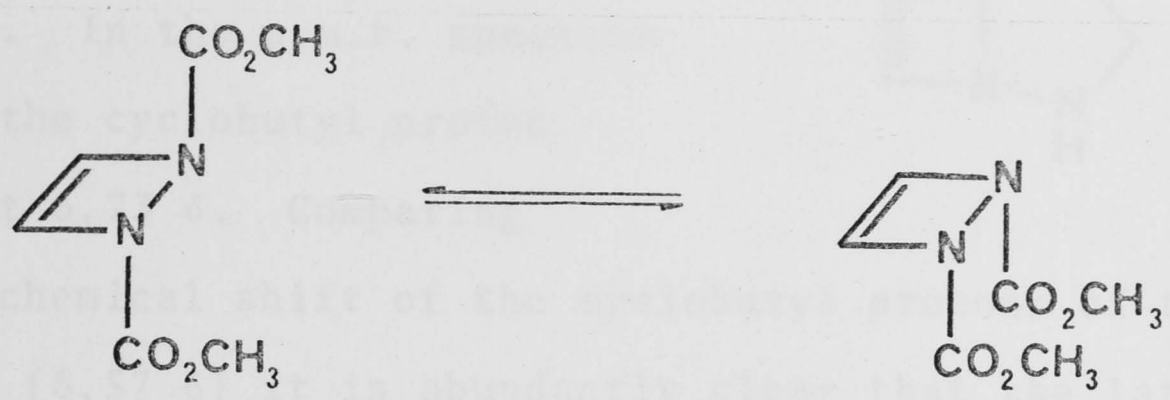
* A peak at *m/e* 174 was thought to arise from a diazetine dimer (*vide infra*).

† CCl_4 solution.

alternatively, may indicate that the molecules exist in two discrete conformations. Recent investigation of related systems has shown that the diacylhydrazine moiety strongly prefers non-eclipsed conformations, with a high activation energy for double nitrogen inversion[69]. In the diazetine, delocalization of the nitrogen lone pair electrons would be expected to substantially lower the activation energy for the inversion process,* though this would not be so in the diazetidine.



The observation that the cyclobutyl (and methyl ester) protons in the p.m.r. spectrum of the diazetidine appear as a sharp singlet supports the suggestion that this compound too undergoes rapid conformational exchange. If these exchange processes were rapid on the n.m.r. time scale (60 MHz) but slow on the i.r. time scale, the spectra would be explained.

Attempts to prepare derivatives of the diazetine with dienes failed, even though electron-rich (cyclopentadiene) and electron-deficient reagents [3,6-di(2'-pyridyl)-*s*-tetrazine] were employed. Such lack of reactivity is reminiscent of aromatic molecules.

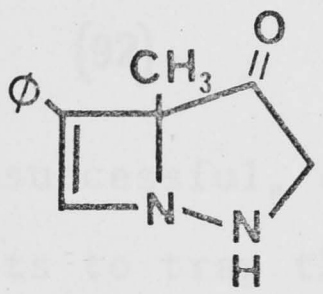
One criterion of aromatic character which has been

---

* Were the delocalization energy sufficient, complete coplanarity would result.

frequently used is the capacity to sustain an induced diamagnetic ring current[70], though difficulty is often experienced in the selection of a model compound for comparison. In the present case, this problem is particularly acute, since simple derivatives of 1-azet-2-ine (90) are unknown. Fortunately, ring-fused derivatives [e.g. (91)] have been prepared[71], and provide a basis for comparison with the diazetine. In the p.m.r. spectrum of (91), the cyclobutyl proton appears at 6.73 δ. Comparing with the chemical shift of the cyclobutyl protons of the diazetine (6.57 δ) it is abundantly clear that the latter is no further downfield than expected from simple inductive effects.* Thus, the diazetine, although a Hückel 6π system, appears incapable of sustaining an induced diamagnetic ring-current, and cannot, by this criterion, be considered "aromatic".

(90)



(91)

It was previously mentioned that the photoproduct was unstable. On storage in solution ($CDCl_3$), the diazetine was slowly transformed [$t_{\frac{1}{2}}$ (20°): 6.9 hrs; $t_{\frac{1}{2}}$ (34°): 1.8 hrs]

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* The difference in chemical shift of the olefinic protons in the diazetine and the ring-fused azetine (0.16 δ) may be attributed to the phenyl group in the latter case. The difference between cyclobutene (5.95 δ)[72] and 1-phenyl-cyclobutene (6.20 δ)[73] is 0.25 δ, while the additive shielding increment of a *cis*-phenyl substituent in olefinic systems is 0.36 δ[74]. The additional ring in (91) is unlikely to have much effect.

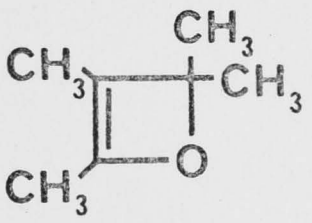
to a new product, whose p.m.r. spectrum displayed only two singlets at 8.36 δ (2H) and 3.98 δ (6H). The mode of formation and the p.m.r. spectrum suggest the 1,4-diazabuta-1,3-diene structure (92), the low field singlet being in the expected position for the imino-aldehyde protons[75].

(84) (92)

Attempts to isolate this product were unsuccessful, owing to its ease of polymerization, while attempts to trap the product with electron-rich olefins such as ethyl vinyl ether also failed.

The extremely facile ring-opening of the diazetine clearly explains why more conventional routes to this ring-system have failed[76]. It is interesting to compare the instability of the diazetine with other unsaturated four-membered heterocycles. Thus thiete (93) has been prepared, but polymerizes slowly at room temperature[77], while the tetramethyloxetene derivative (94), though not isolable, has been shown to ring-open to the corresponding pentenone with a half-life of 12 hrs at 37°[78].

(93)



(94)

The greater instability of the diazetine clearly demonstrates that if electron delocalization is present in this molecule, then little overall stabilization results.

SECTION C

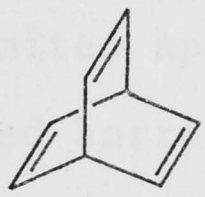
THE PHOTOCHEMICAL SYNTHESIS OF BARRELENE DERIVATIVES

ABSTRACT

The 1,2-photoaromatization reaction has been successfully applied to the synthesis of benzo- and dibenzobarrelenes. Modification of the approach has allowed preparation of dihydrobarrelenes, though extension to the parent barrelene system was frustrated by competing reactions.

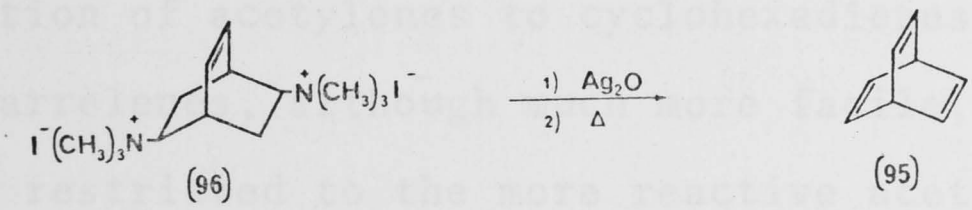
INTRODUCTION

Interest in the bicyclo[2.2.2]octa-2,5,7-triene (barrelene) system (95) originated from the suggestion that the six π electrons might be delocalized in a cylindrical ("barrel-shaped") arrangement giving rise to aromatic character[79]. Synthesis of the parent compound and MO calculations, however, indicated that although the electrons occupy delocalized molecular orbitals, little overall delocalization energy is present and no abnormal stability results[80].



(95)

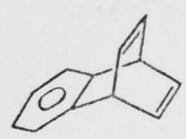
The parent hydrocarbon (95) was first obtained in 1960 by an 8-step synthesis culminating in double Hofmann elimination from the quaternary ammonium salt (96)[81].



(96) (95)

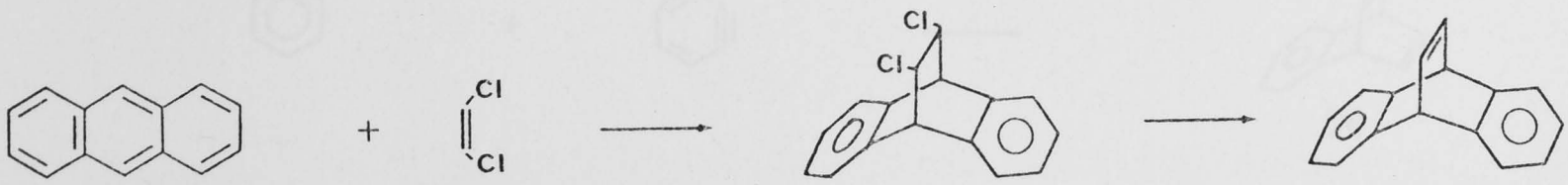
Similar routes have been employed in the synthesis of dihydrobarrelene (97)[82] and benzobarrelene (98)[83].

(97)



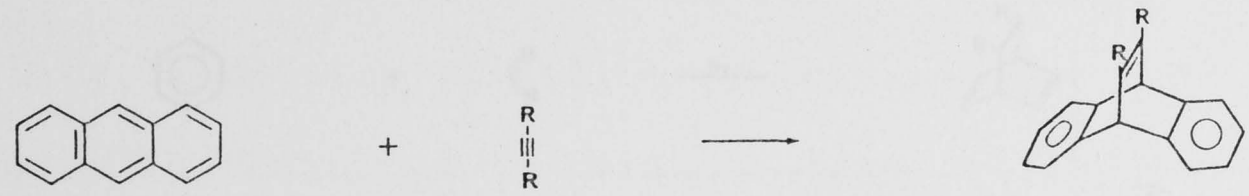
(98)

Dibenzobarrelenes (e.g. 99a) have also been prepared by a route involving an elimination as the final step. Addition of 1,2-dichloroethylene to anthracenes gave adducts which yielded dibenzobarrelenes on dechlorination[84].



(99a)

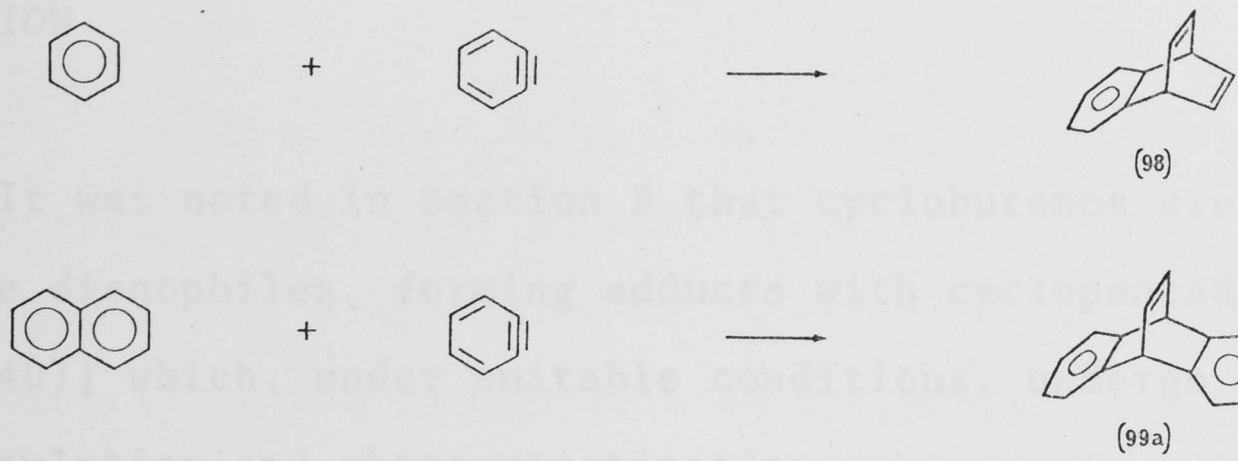
Direct thermal addition of acetylenes to benzenes, naphthalenes and anthracenes is of very limited application to the synthesis of the parent and annelated barrelenes, as only acetylenes bearing strongly electron-withdrawing substituents (e.g. CF_3, CN, CO_2R) have been successfully employed[85-89]. The reported preparation of dibenzobarrelene by addition of acetylene to anthracene has never been repeated[90].



Addition of acetylenes to cyclohexadienes, as a route to dihydrobarrelenes, although much more facile, is also effectively restricted to the more reactive acetylenes owing to the limited thermal stability of these products[85,87,91].

Benzo- and dibenzobarrelenes have also been prepared by addition of benzynes to benzenes and naphthalenes. However,

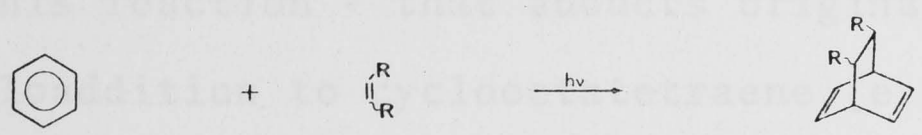
the reaction gives complex mixtures from which only poor yields of the 1,4-adducts can be isolated[92], except when tetrahalobenzynes are employed[93].



(98)

(99a)

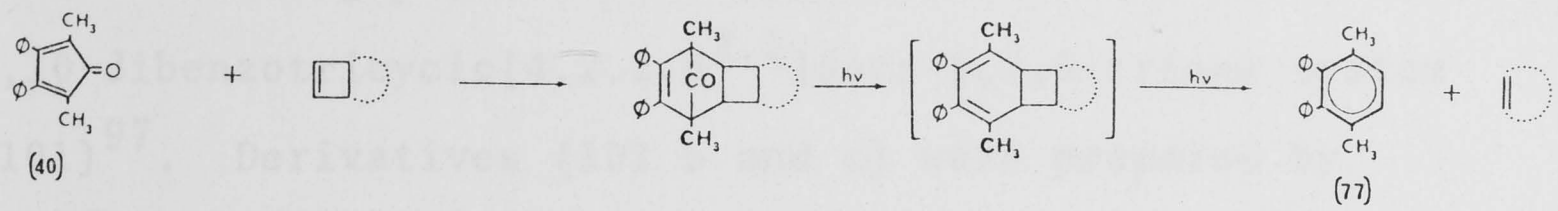
Photochemical 1,4-addition of olefins to benzene has been used to prepare dihydrobarrelenes, but the reaction is complicated by competing 1,2- and 1,3-additions. Only *cis*- and *trans*-but-2-ene[94] and 1,2-dichlorovinylene carbonate[95] have been successfully employed.



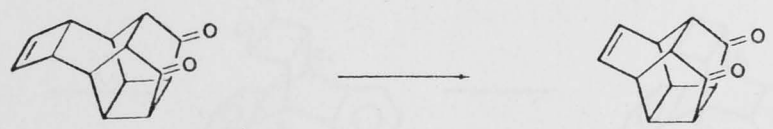
Considerable interest has been shown in the novel photochemical transformations of barrelene and its annelated analogues, as part of the general study of $(CH)_8$ interconversions[96]. A significant feature of the 1,2-photoaromatization route to these derivatives is that it demonstrates that a photochemical reaction can be employed to generate compounds known to be photolabile.

DISCUSSION

It was noted in Section B that cyclobutenes are reactive dienophiles, forming adducts with cyclopentadienones [e.g. (40)] which, under suitable conditions, undergo decarbonylation and photoaromatization.

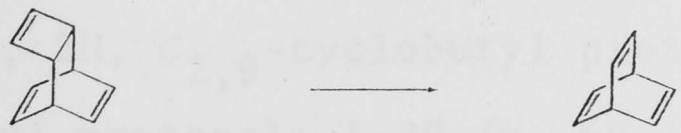


The conversion of the cyclobutene (24) to the olefin (25) mentioned in the Introduction demonstrates an important feature of this reaction - that adducts originating from (4 + 2)π cycloaddition to cyclooctatetraene [e.g. (24)] can be readily converted to products [e.g. (25)] formally derived from 1,4-addition to benzene, a reaction rarely observed[1].



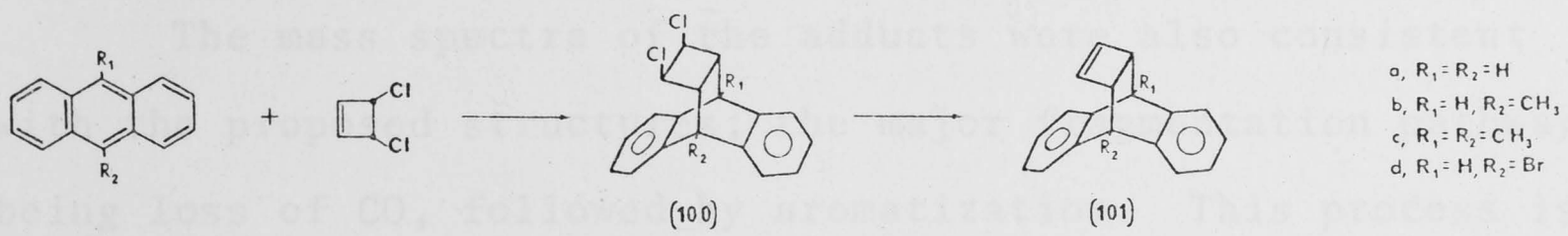
(24) (25)

The proposed synthesis of bicyclo[2.2.2]octa-2,5,7-triene systems from the corresponding tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene derivatives is a logical extension of these ideas.



The reaction sequence was first applied to the synthesis of dibenzobarrelenes. The generality of the reactions was established by the preparation of mono- and di-substituted derivatives (99 b and c), as well as the parent hydrocarbon (99a).

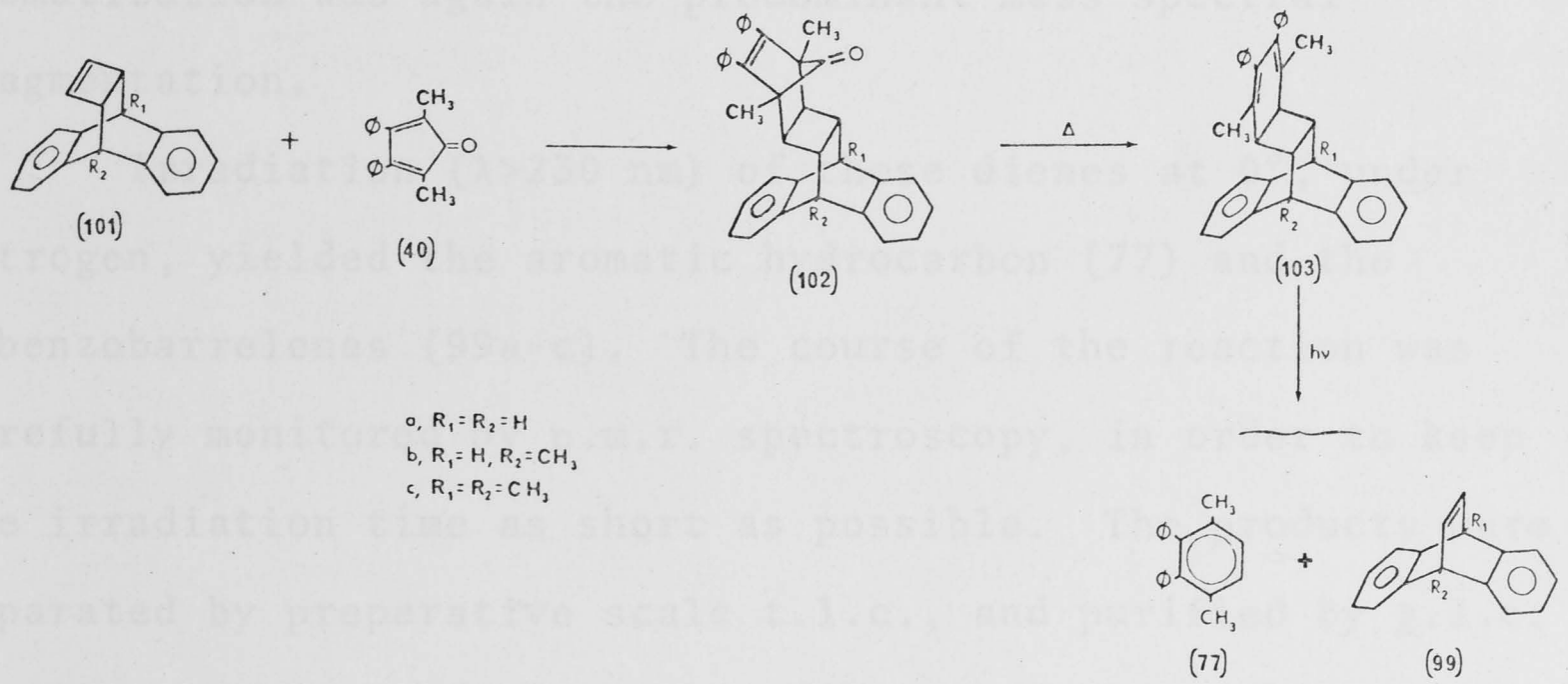
Starting point of the synthesis was the known 7,8; 9,10-dibenzotricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene system (101)[97]. Derivatives (101 b and c) were prepared by dechlorination of the adducts (100 b and c) resulting from addition of *cis*-3,4-dichlorocyclobutene to 9-methyl- and 9,10-dimethylanthracene respectively. For the synthesis of (101a), 9-bromoanthracene was employed, the bromine atom in the resulting adduct (100d) being replaced by hydrogen in the dehalogenation step. Sodium dihydronaphthylide[98] was found to be a better reagent than zinc or lithium amalgam in effecting dehalogenation in these systems[97].



(100) (101)

Treatment of the cyclobutenes (101a-c) with 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone (40) in refluxing benzene gave the adducts (102a-c) in good yield. The bridge-ketone structure in each case was fully supported by spectral data, that of (102a) being typical: λ_{max} (EtOH) 250, 267, 273

nm, ε 9200, 10700, 10300; p.m.r. ($CDCl_3$, δ p.p.m.): 7.5-6.8 (m, 18H, aromatic protons); 4.35 (m, 2H, $C_{1,10}$-bridgehead protons); 2.20 (m, 2H, $C_{2,9}$-cyclobutyl protons); 1.67 (m, 2H, $C_{3,8}$-cyclobutyl protons); 1.20 (s, 6H, $C_{4,7}$-methyl protons); ν_{max} 1770 cm^{-1}. Only one isomer was formed in each case, the *exo*, *anti* stereochemistry depicted being expected from addition of the dienone onto the least hindered side of the cyclobutenes. A preference for *exo* addition has been observed in (4 + 2)π cycloadditions of cyclobutenes[63]. *anti* Stereochemistry was supported by the observed lack of coupling between the cyclobutyl protons in the p.m.r. spectrum[65].



The mass spectra of the adducts were also consistent with the proposed structures; the major fragmentation pathway being loss of CO, followed by aromatization. This process is of course precisely that required for the photochemical formation of dibenzobarrelenes.

Photochemical breakdown of the adduct (102c) did indeed parallel the mass spectral fragmentation, but was complicated by competing reactions, the yield of 1,4-dimethyl-2,3-diphenylbenzene (77) and 1,4-dimethyldibenzobarrelene (99c)

amounting to only 30%. The diene (103c) was the presumed intermediate, being detectable in p.m.r. spectra recorded at initial stages of the photolysis.

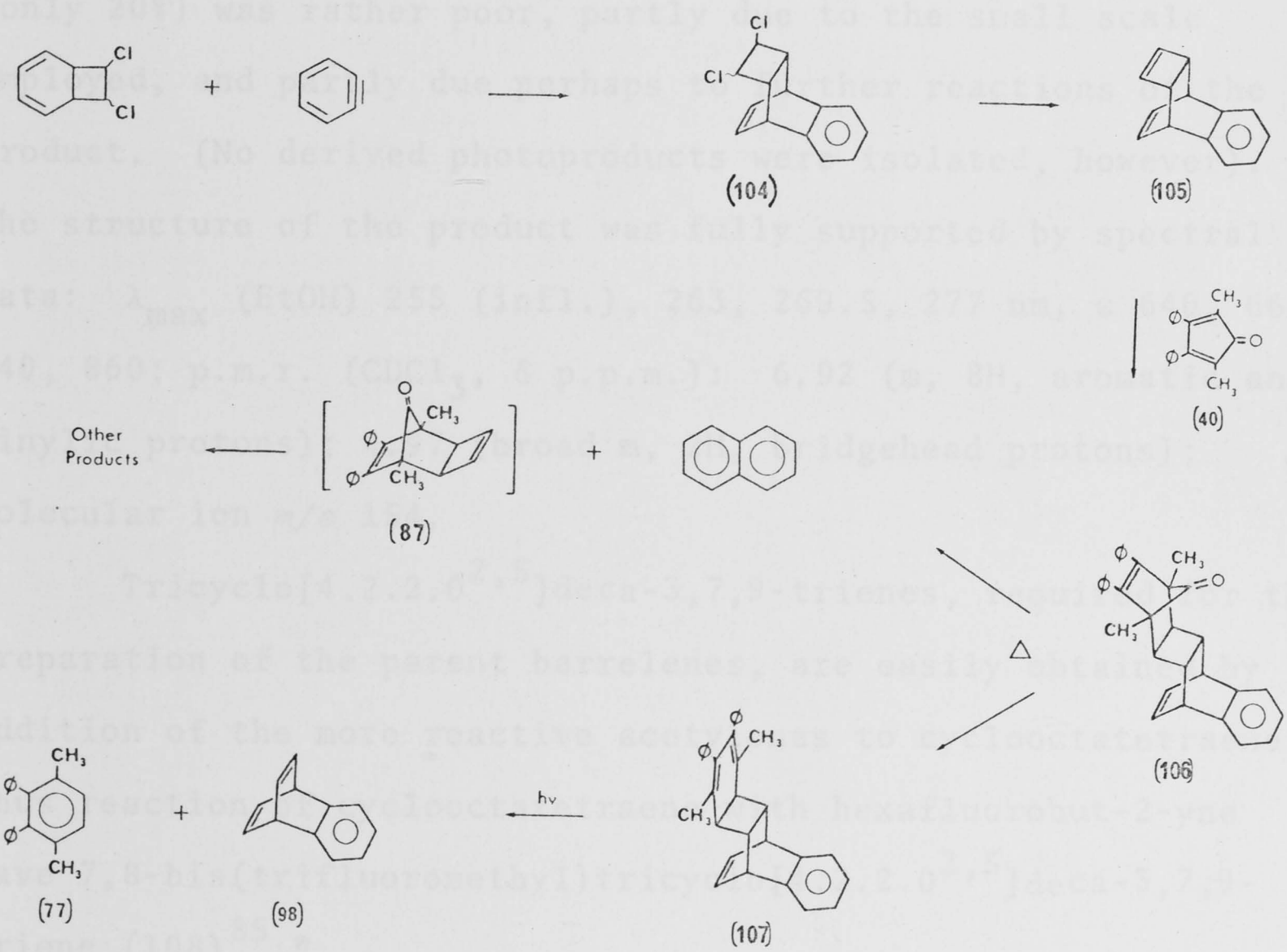
It was subsequently found that the dienes (103) could be formed from the ketones (102) by thermal elimination of the bridging carbonyl group[99]. Again the structure of the products was supported by analytical and spectral data [e.g. (103a): λ_{max}(EtOH) 247, 266(infl.), 274, 305(infl.) nm, ε 11500, 7800, 6700, 3200; p.m.r. ($CDCl_3$, δ p.p.m.): 7.5-6.6 (m, 18H, aromatic protons); 4.43 (m, 2H, $C_{1,10}$-bridgehead protons); 2.72 (m, 2H, $C_{2,9}$-cyclobutyl protons); 2.14 (m, 2H, $C_{3,8}$-cyclobutyl protons); 1.47 (s, 6H, $C_{4,7}$-methyl protons)]. Aromatization was again the predominant mass spectral fragmentation.

Irradiation (λ>230 nm) of these dienes at 0°, under nitrogen, yielded the aromatic hydrocarbon (77) and the dibenzobarrelenes (99a-c). The course of the reaction was carefully monitored by p.m.r. spectroscopy, in order to keep the irradiation time as short as possible. The products were separated by preparative scale t.l.c., and purified by g.l.c. The u.v. spectrum of the parent dibenzobarrelene (λ_{max} 252, 258.5 (infl.), 266, 272.5, 279.5 nm, ε 1600, 870, 1050, 2200, 3400) correlated well with published data[100], the spectra of all the products being consistent with the proposed structures.

Although no photoproducts derived from the dibenzobarrelenes were observed (dibenzocyclooctatetraenes or dibenzosemibullvalenes might be expected[85]), the yield of dibenzobarrelenes in each case appeared to depend on the difference between its rate of formation and its rate of photochemical conversion to other products. The difference was greatest for the disubstituted derivative (99c), which

was thus obtained in higher yield (72%) than (99b) (69%) or (99a) (48%).

The reaction sequence was next applied to the synthesis of benzobarrelene (98). The starting cyclobutene, 7,8-benzotricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (105) was prepared by dechlorination, with disodium dihydrophenanthrenedi-ide, of the adduct (104) of benzyne and 7,8-dichlorobicyclo[4.2.0]-octa-2,4-diene[101].



Reaction with the dienone (40) gave the adduct (106) in good yield. Two isomers were formed (ratio *ca.* 10:1), the major isomer as before being thought to have the *exo, anti* stereochemistry depicted.

Brief heating at the melting point (245°) converted the ketone (106) to the diene (107), whose structure was fully supported by analysis and by spectral data. A small amount (*ca.* 5%) of naphthalene present in the crude pyrolysate

was due to competing (4 + 2)π cycloreversion. The other product, *exo*-1,6-dimethyl-7,8-diphenyltricyclo[4.2.1.$0^{2,5}$]nona-3,7-dien-9-one (87) was not observed, being unstable at this temperature.

Ultraviolet irradiation of the diene (107) was performed under conditions similar to those used successfully for the preparation of the dibenzobarrelenes. The irradiation was stopped after 75% reaction, to avoid excessive decomposition of the benzobarrelene (98), which was separated by preparative scale t.l.c. and sublimation. The isolated yield in this case (only 20%) was rather poor, partly due to the small scale employed, and partly due perhaps to further reactions of the product. (No derived photoproducts were isolated, however). The structure of the product was fully supported by spectral data: λ_{max} (EtOH) 255 (infl.), 263, 269.5, 277 nm, ε 640, 660, 840, 860; p.m.r. ($CDCl_3$, δ p.p.m.): 6.92 (m, 8H, aromatic and vinylic protons); 4.97 (broad m, 2H, bridgehead protons); molecular ion *m/e* 154.

Tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-trienes, required for the preparation of the parent barrelenes, are easily obtained by addition of the more reactive acetylenes to cyclooctatetraene. Thus reaction of cyclooctatetraene with hexafluorobut-2-yne gave 7,8-bis(trifluoromethyl)tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (108)[85].*

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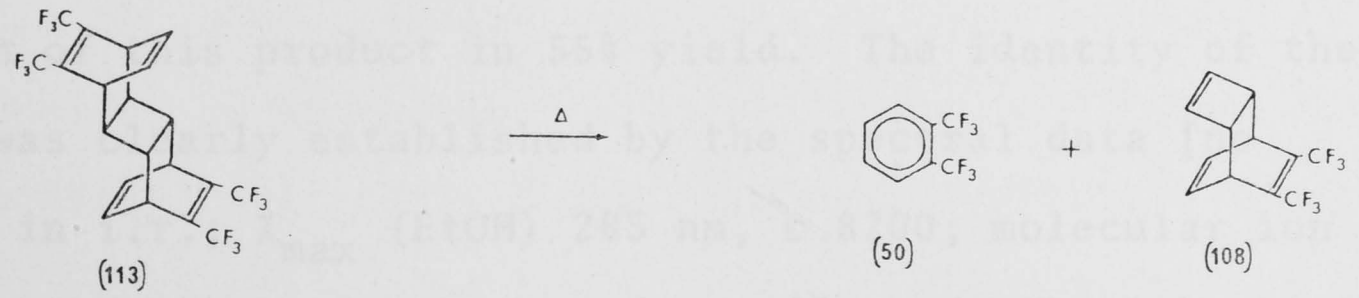
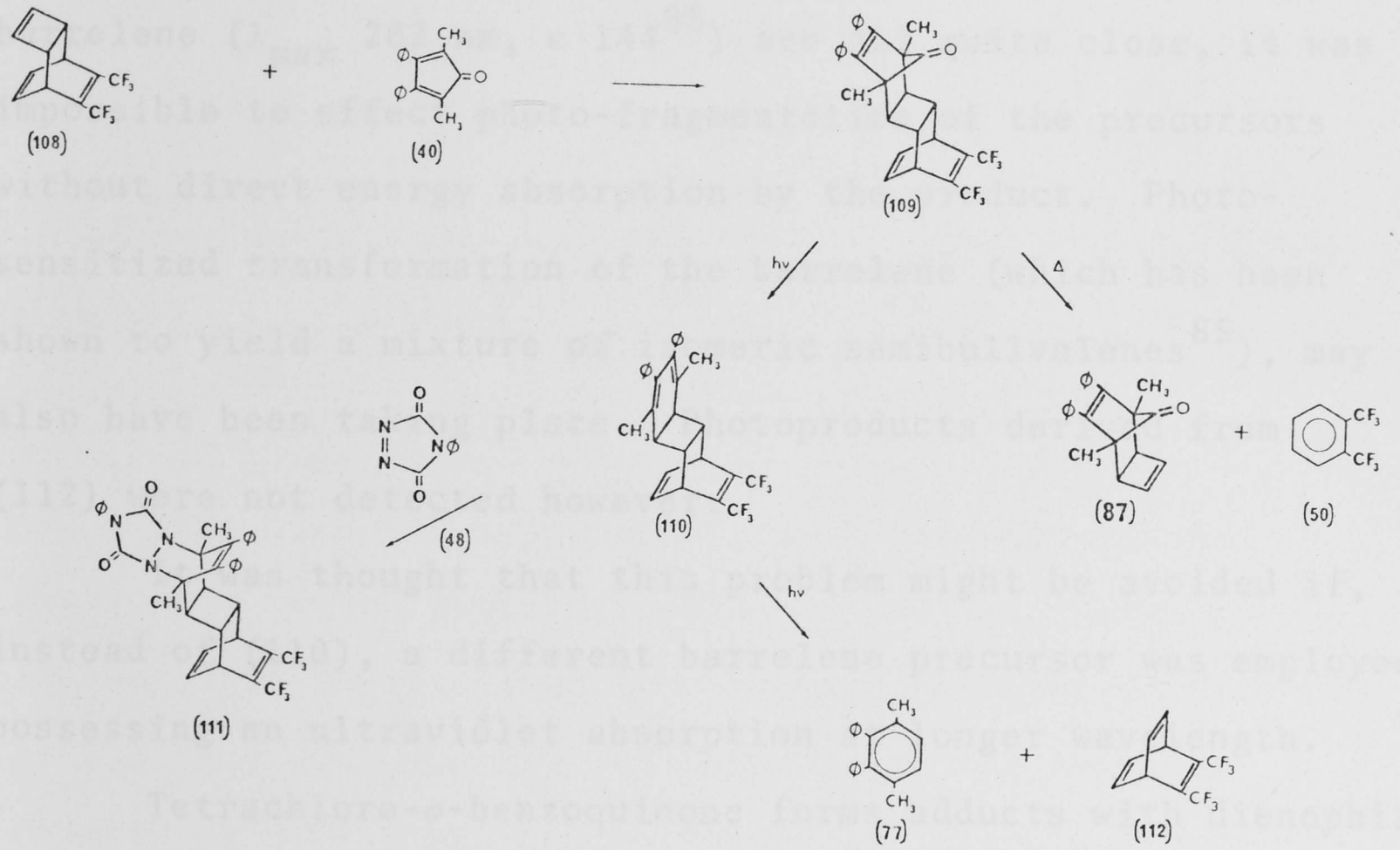
* The reaction also gave the crystalline product (113), whose structure and stereochemistry followed from analytical and spectral data, and from controlled pyrolysis to (50) and (108).



(113) (50) (108)

The product is thought to be derived from a cyclooctatetraene dimer[102], but it is uncertain at this stage which is involved.

The cyclobutene (108) reacted readily with the dienone (40) giving two adducts (ratio 5:1). The *exo, anti* stereochemistry of the major adduct (109) was established by controlled pyrolysis at the melting point, which yielded *o*-bis(trifluoromethyl)benzene (50) and the known *exo*-1,6-dimethyl-7,8-diphenyltricyclo[4.2.1.$0^{2,5}$]nona-3,7-dien-9-one (87)[63]. Decarbonylation to the diene (110) did not occur in this case, owing to the greater ease of the (4 + 2)π cycloreversion.



The diene (110) was formed however by photochemical elimination of the bridging carbonyl group of (109). Although susceptible to further photochemical reaction, careful monitoring of the reaction (by p.m.r. spectroscopy) allowed isolation of this product in 55% yield. The identity of the product was clearly established by the spectral data [no carbonyl in i.r.; λ_{max} (EtOH) 285 nm, ε 8200; molecular ion *m/e* 498], and by the formation of an adduct (111) with

4-phenyl-1,2,4-triazoline-3,5-dione (48).

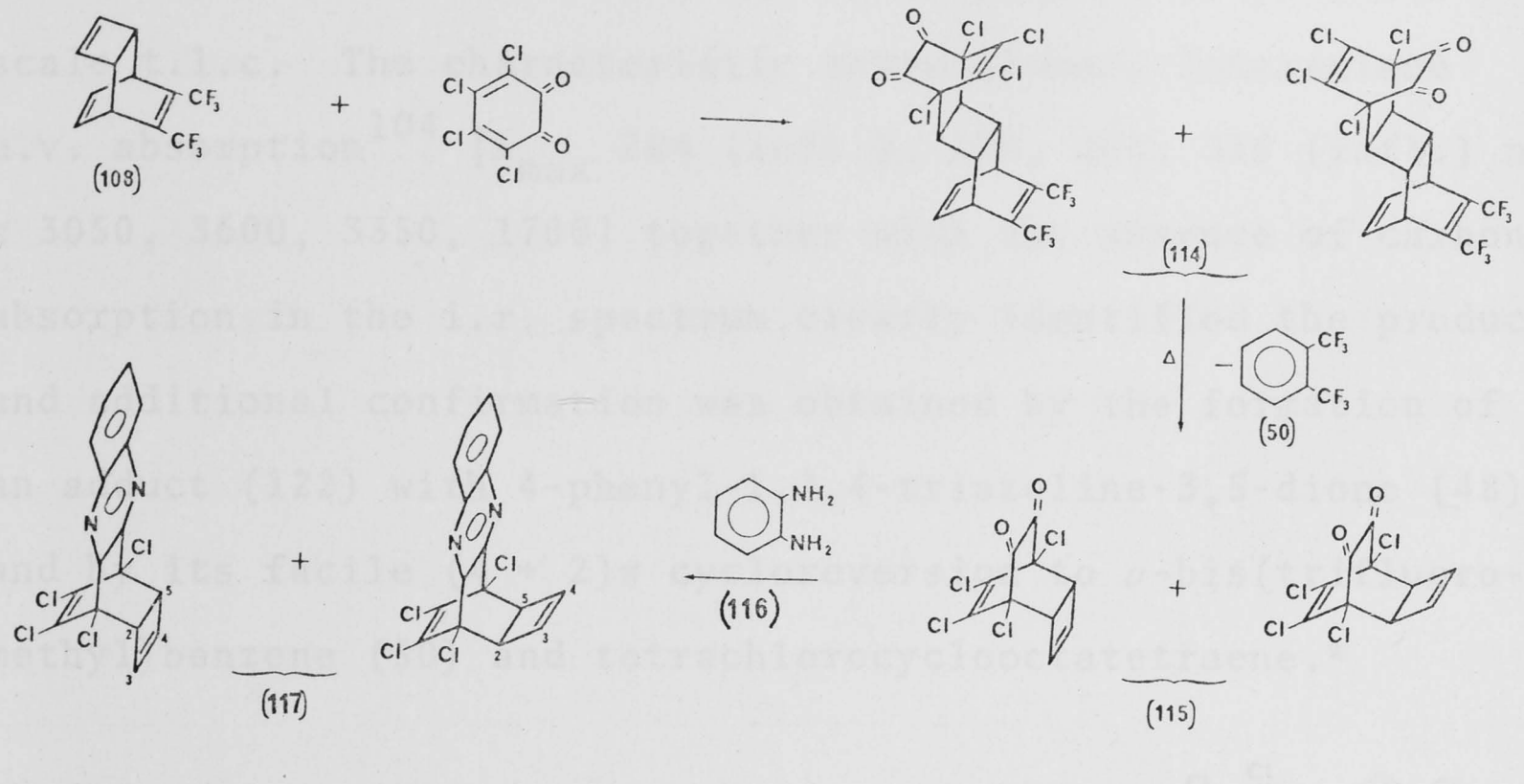
Ultraviolet irradiation of the diene (110), or prolonged irradiation of the ketone (109) produced 1,4-dimethyl-2,3-diphenylbenzene (77), but although a number of different solvents and filters were used, 2,3-bis(trifluoromethyl)-bicyclo[2.2.2]octa-2,5,7-triene (112), the other expected photoproduct, was never present in more than trace amounts. This appeared to be due to facile photochemical decomposition of this product. Since the absorption maxima of the ketone (λ_{max} 261 nm, ε 8900), the diene (λ_{max} 285 nm, ε 8200) and the barrelene (λ_{max} 262 nm, ε 144[85]) are all quite close, it was impossible to effect photo-fragmentation of the precursors without direct energy absorption by the product. Photo-sensitized transformation of the barrelene (which has been shown to yield a mixture of isomeric semibullvalenes[85]), may also have been taking place. Photoproducts derived from (112) were not detected however.

It was thought that this problem might be avoided if, instead of (110), a different barrelene precursor was employed possessing an ultraviolet absorption at longer wavelength.

Tetrachloro-*o*-benzoquinone forms adducts with dienophiles, from which the α-diketone bridge may be photochemically eliminated yielding tetrachlorocyclohexadienes[103]. Since this chromophore typically absorbs ultraviolet light at wavelengths up to 325 nm[104], it was thought that adducts of the quinone and tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-trienes might serve as precursors for the photochemical synthesis of barrelenes.

Addition of tetrachloro-*o*-benzoquinone to 7,8-bis-(trifluoromethyl)tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (108), though not rapid, proceeded smoothly and yielded a product (114) whose uniform bright yellow colour [λ_{max} ($CHCl_3$) 438 nm,

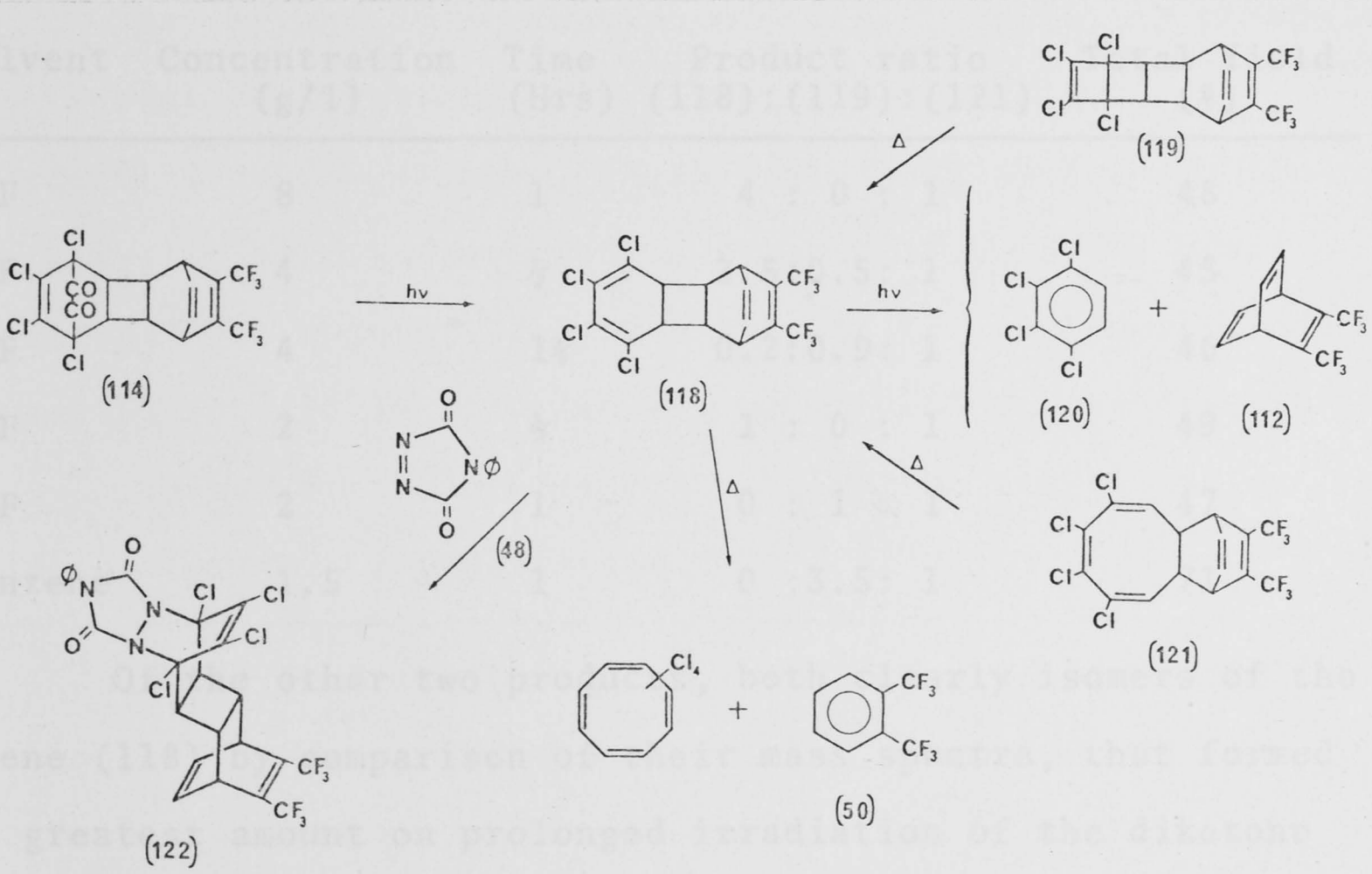
ε 145] and i.r. spectrum (ν_{max} 1762, 1772 cm^{-1}) were clearly consistent with an α-diketone structure. P.m.r. spectroscopy, however, suggested that the product was a 4:3 mixture of *exo* and *endo* isomers, though these were not separable by t.l.c. (owing to the extreme ease of hydration on silica) or by fractional recrystallization.



This view was supported by controlled pyrolysis experiments, which yielded, besides *o*-bis(trifluoromethyl)-benzene (50), a mixture of isomeric cyclobutenes (115). The i.r. and u.v. spectra were similar to the original product, showing that the α-diketone structure had been retained, and this was confirmed by condensation with *o*-phenylenediamine (116), which produced a mixture of isomeric quinoxalines (117). Careful comparison of the p.m.r. spectra of these derivatives with those of the cyclobutenes allowed assignment of *endo* stereochemistry to the major adduct in each case, by observing that the C_2 and C_5 cyclobutyl protons of the major quinoxaline isomer were shielded (by 0.17 p.p.m.) relative to the major cyclobutene, while the C_3 and C_4 olefinic protons of the minor quinoxaline isomer were shielded

(by 0.32 p.p.m.) relative to the minor cyclobutene. A preference for *endo* addition has been noted in reactions of quinones with dienophiles[105].

Irradiation (λ>300 nm) of the α-diketone adduct (114) in THF, under nitrogen, resulted in smooth decarbonylation. The diene (118) was the major product on brief irradiation in more concentrated solutions, and was separated by preparative scale t.l.c. The characteristic tetrachlorocyclohexadiene u.v. absorption[104] [λ_{max} 284 (infl.), 294, 304, 319 (infl.) nm, ε 3050, 3600, 3350, 1700] together with the absence of carbonyl absorption in the i.r. spectrum clearly identified the product, and additional confirmation was obtained by the formation of an adduct (122) with 4-phenyl-1,2,4-triazoline-3,5-dione (48), and by its facile (4 + 2)π cycloreversion to *o*-bis(trifluoromethyl)benzene (50) and tetrachlorocyclooctatetraene.*



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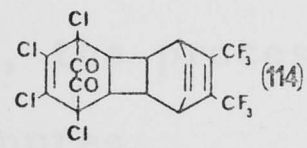
* A 3:2 mixture of 1,2,3,4- and 1,2,3,8-tetrachlorocyclooctatetraenes was in fact produced, but these compounds are discussed fully in Section D.

Irradiation of the diene (118), or prolonged irradiation of the α-diketone (114) in dilute THF or benzene solution resulted in the formation of 1,2,3,4-tetrachlorobenzene (120) and 2,3-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene (112), the expected photoaromatization products, and two other compounds whose t.l.c. behaviour was so similar to the diene (118) that they were separated only with difficulty. Unfortunately, even under a variety of conditions (see Table 2), the yield of photoaromatization products never amounted to more than 12%. Thus isolation and positive identification of the barrelene (112) was not possible, though it was identifiable in p.m.r. spectra of the crude photolysate.

TABLE 2

Photolyses of  (114)

Solvent	Concentration (g/l)	Time (Hrs)	Product ratio (118):(119):(121)	Total Yield (%)
THF	8	1	4 : 0 : 1	48
THF	4	½	2.5:0.5: 1	45
THF	4	1¼	0.2:0.9: 1	46
THF	2	½	1 : 0 : 1	49
THF	2	1	0 : 1 : 1	47
Benzene	1.5	1	0 :3.5: 1	71

Of the other two products, both clearly isomers of the diene (118) by comparison of their mass spectra, that formed in greatest amount on prolonged irradiation of the diketone in dilute solution, or more rapidly in benzene solution, was assigned the pentacyclic structure (119), this being consistent with the absence of absorption in the u.v. spectrum. The other isomer, the major product at intermediate concentration

and irradiation time, was assigned structure (121). The presence of a cyclooctatriene ring was indicated by the p.m.r. spectrum which included similar multiplets at 5.75 δ (2H, $C_{3,8}$-olefinic protons) and at 2.99 δ (2H, $C_{2,9}$-protons), and by the u.v. spectrum, which showed a maximum at 245 nm (ε 6800) with tailing up to 300 nm.

Both these products were found to be thermally labile, the cyclooctatriene especially so. Irreversible conversion to the diene (118) was rapid at 100°, and occurred within a few seconds at its melting point (130°), while at 80°, in deuteriochloroform solution, the conversion was first-order, with a half-life of 27 minutes. The other photoproduct was also converted to (118) on heating, but much more slowly. At 140° in chloroform solution, the process was again first-order, and the half-life was 44 minutes.

The thermal isomerization of (121) to (118) is consistent with recent observations of cyclooctatriene - bicyclo[4.2.0]-octadiene interconversions, which have shown that formation of the bicyclic form is favoured by substitution in the 7 and 8 positions[106]. However, the stability of the cyclooctatriene isomer (up to 50° in solution and up to 130° in the crystalline state) implies that a substantial activation energy is required for this isomerization.*

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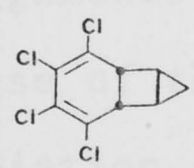
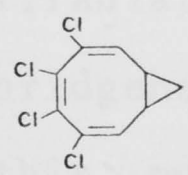
* (123) and (124) exhibit a reversed order of stability[22], presumably due to additional strain associated with the fused cyclopropyl ring.



(123)



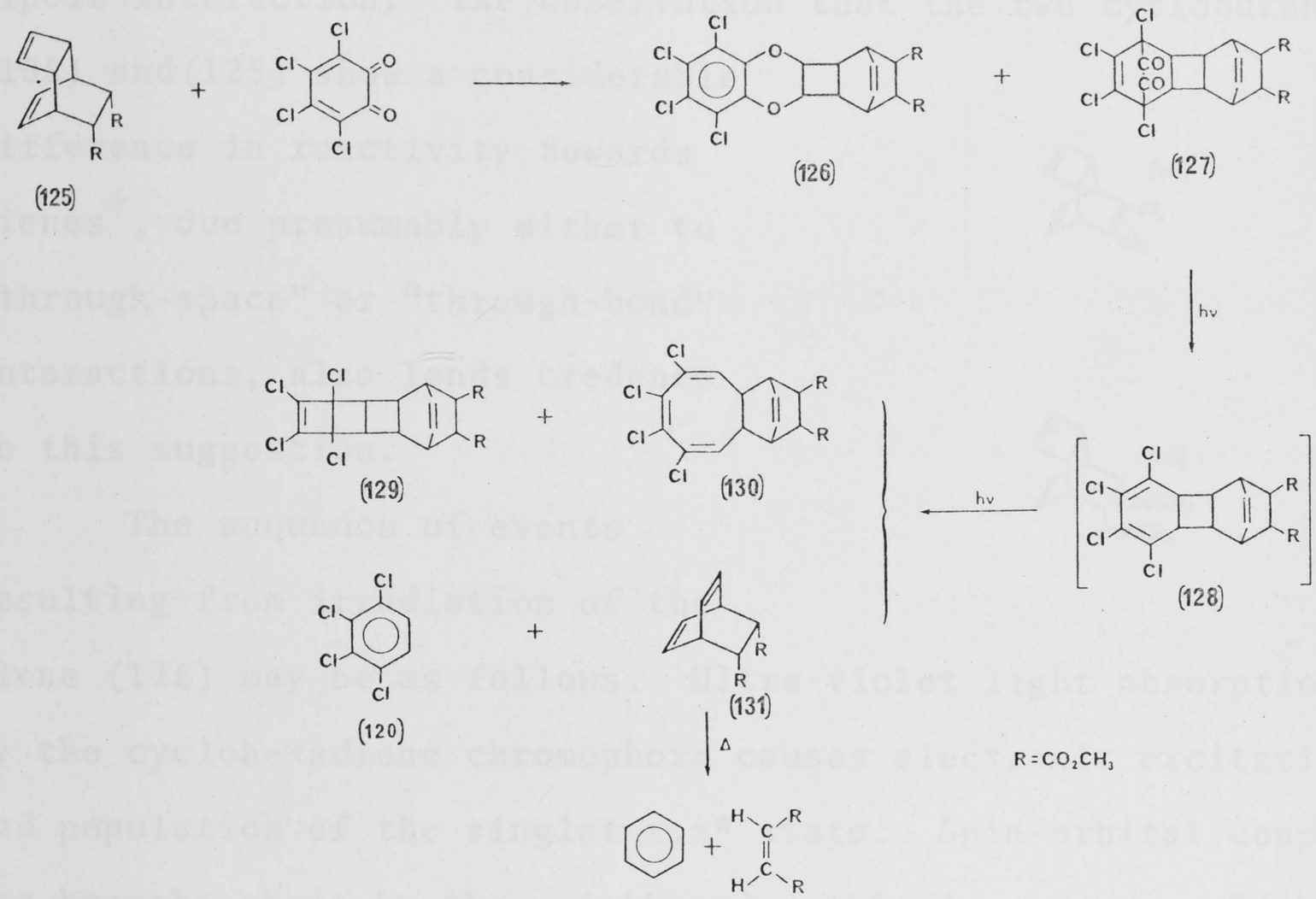
(124)

That ring-opening and ring-closure reactions should be preferred to aromatization was unexpected, but the reasons for this are discussed more fully later.

Preliminary investigations conducted by Dr. W.S. Wilson[107] have indicated that 1,2-photoaromatization does occur on irradiation of the diketone (127). However, the product, 2,3-*cis*-dimethoxycarbonyl-bicyclo[2.2.2]octa-5,7-diene (131) was not obtained in the pure state, or completely characterized. Since this observation appeared to be at variance with the results obtained in the related series discussed previously, this work was repeated.

Accordingly, the diketone (127) was prepared from tetrachloro-*o*-benzoquinone and the cyclobutene (125), care being taken to separate this adduct from the dioxene isomer (126) also formed. Irradiation of the diketone was performed in benzene solution (solubility in THF was slight) under nitrogen, and the products were separated by preparative scale t.l.c. 1,2,3,4-Tetrachlorobenzene (120) and the dihydro-barrelene (131) were each formed in good yield (65%). The latter, a colourless crystalline solid, was unambiguously identified by its mass spectrum (molecular ion *m/e* 222), by analysis, and by its p.m.r. spectrum ($CDCl_3$) which showed two overlapping quartets centred at 6.5 δ (4H, $C_{5,6,7,8}$-vinylic protons), a broad multiplet at 3.93 δ (2H, $C_{1,4}$-bridgehead protons), and singlets at 3.66 δ (6H, *O*-methyl protons) and 2.95 δ (2H, $C_{2,3}$-protons). Spin decoupling experiments confirmed these assignments. Irradiation in the vinylic region caused collapse of the bridgehead multiplet to a singlet, while irradiation at this position caused the vinylic quartets to collapse to two singlets. Although indefinitely stable at room temperature (samples were stored

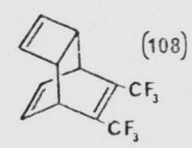
for 6 months without change), facile stereospecific (4 + 2)π cycloreversion to benzene and dimethyl maleate occurred on warming. The half-life of this first-order process (in deuteriochloroform solution) was 6 hours at 60°. In few instances has the stereospecificity of concerted (4 + 2)π cycloreversions been so convincingly demonstrated[88].

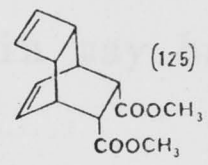


The photolysis also produced compounds (129) and (130), which were readily identified by comparison with the previously-mentioned analogues. Again, these were thought to be formed from the diene (128), but in this case the intermediate was not isolated.

That 1,2-photoaromatization occurs readily in this, but not in the previous case, appears to be due to interaction between the tetrachlorocyclohexadiene chromophore

and the remote olefinic centre in (118)*. No evidence for such an interaction was detectable in the u.v. spectrum of this compound, though comparison of the u.v. spectra of the diketones (114) [λ_{max} ($CHCl_3$) 282, 438 nm, ε 725, 145] and (127) [λ_{max} ($CHCl_3$) 272, 438 nm, ε 2240, 310] revealed a hypochromic effect in the former which may be due to dipole-dipole interaction. The observation that the two cyclobutenes (108) and (125) show a considerable difference in reactivity towards dienes†, due presumably either to "through-space" or "through-bond" interactions, also lends credence to this suggestion.





The sequence of events resulting from irradiation of the diene (118) may be as follows. Ultra-violet light absorption by the cyclohexadiene chromophore causes electronic excitation and population of the singlet π,π* state. Spin-orbital coupling brought about by the neighbouring chlorine atoms would be expected to promote rapid intersystem crossing (radiationless conversion) to the corresponding triplet state[108]. The various photochemical reactions would then have to compete

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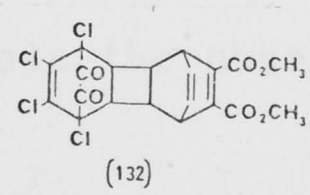
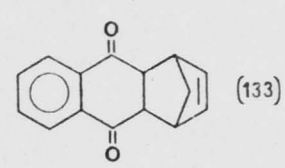
* Preliminary photolysis experiments with (132) indicate that 1,2-photoaromatization is a minor reaction in this case also.



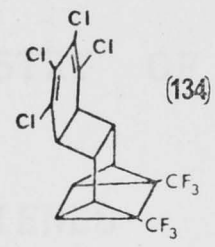
(132)

† Although quantitative measurements have not been undertaken, reaction of tetrachloro-*o*-benzoquinone for example with (125) appears to be approximately four to five times more rapid than with (108).

with other deactivation processes. Intermolecular triplet energy transfer is unlikely in dilute solution. Intramolecular triplet energy transfer to the remote olefinic centre is entirely feasible however, provided that the donor chromophore has the higher energy[109]. Unfortunately, no estimate of these energies is available. Intramolecular triplet energy transfer from the diketone chromophore to the norbornylene double bond has been shown to precede cage formation in the cyclopentadiene adduct (133)[110].


(133)

Absorption of energy by the remote olefin may have been expected to result in (2 + 2)π closure of the bicyclo[2.2.2]-octadiene moiety yielding (134). (No evidence for such an intermediate was found). However, it has been shown that this process cannot be triplet-sensitized[111], implying that the excited singlet state is required. Since the available evidence suggests that 1,2-photoaromatization is a triplet process[11], while the competing intramolecular ring-closure and ring-opening reactions are singlet processes[112], triplet energy quenching by the remote olefinic centre would satisfactorarily explain the observed product distributions.*


(134)

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* The products cannot be derived from "hot" ground-state diene molecules, since the diene is thermodynamically more stable.

SECTION D

THE SYNTHESIS AND PHOTOCHEMISTRY OF

BICYCLO[4.2.0]OCTA-2,4,7-TRIENES

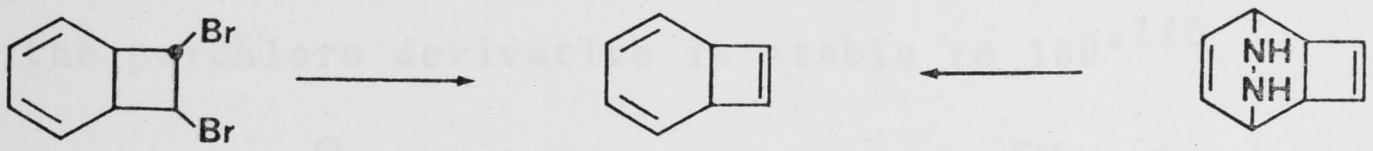
ABSTRACT

2,3,4,5-Tetrachlorobicyclo[4.2.0]octa-2,4,7-triene has been synthesized by the photochemical decarbonylation of *exo*- and *endo*-1,6,9,10-tetrachlorotricyclo[4.2.2.$0^{2,5}$]deca-3,9-dien-7,8-dione. The thermal and photochemical transformations of this compound are discussed, with special reference to the orbital-symmetry requirements of the processes involved.

INTRODUCTION

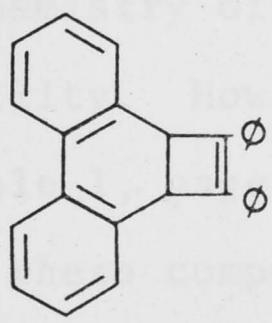
Although biCOTs* have long been suggested as intermediates in the addition of dienophiles to COTs[113], and in the photoaddition of acetylenes to benzenes[114], only in the last few years have these interesting compounds become available for direct study.

The parent hydrocarbon (1), originally prepared by low-temperature debromination of the COT dibromide (135)[115], and more recently by mild oxidation of the hydrazine (136)[116], readily undergoes isomerization to COT, even below 0°, adequately explaining why earlier synthetic attempts had failed.



(135) (1) (136)

Benzo and dibenzo derivatives [e.g. (137)], which may be prepared by direct photochemical addition of the appropriate acetylene and aromatic hydrocarbon[117], are much more stable since



(137)

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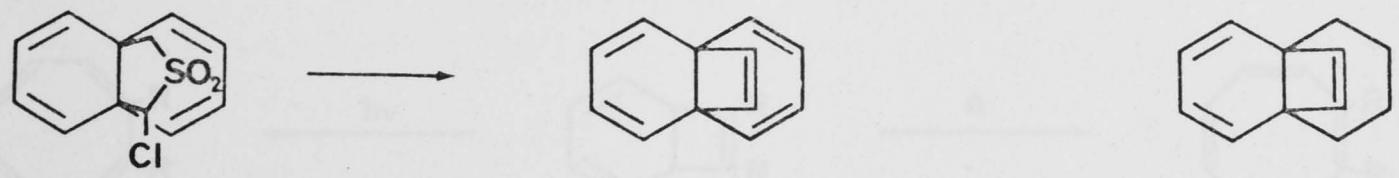
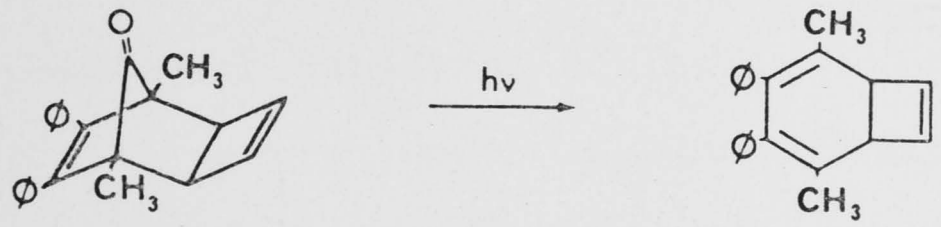
* In this Section it will be found convenient to use the abbreviations COT (cyclooctatetraene) and biCOT (bicyclo[4.2.0]octa-2,4,7-triene).

symmetry-controlled concerted ring-opening would require the initial formation of unfavourable *o*-xylylene or quinonoid systems. The novel [4.4.2]propellapentaene analogue (7), prepared by Ramberg-Bäcklund rearrangement of the α-chlorosulphone (138), also exhibited considerable thermal stability due to the constraining effect of the additional cyclohexadiene ring[6]. The propellatriene derivative (6) behaved in a similar fashion[5].



(138) (7) (6)

The biCOT ring-system is also stabilized by simple substitution, particularly in the cyclohexadiene ring[118]. The 2,5-dimethyl-3,4-diphenyl derivative (3) for example, prepared by photochemical decarbonylation of the tricyclic ketone (87)[119], exhibits appreciable stability at 65°, while the perchloro derivative is stable to 160°[120].



(87) (3)

Systematic study of the photochemistry of biCOTs has been hampered by this lack of availability. However, as mentioned in the Introduction (see Table 1, page 2), in all cases so far studied,* irradiation of these compounds has

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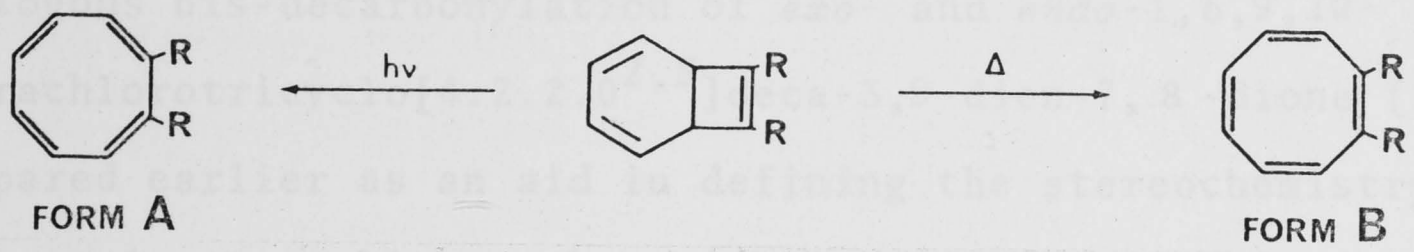
* The photochemistry of the benzo derivatives[121] bears no relationship to that of the parent system.

resulted in 1,2-photoaromatization, with formation of benzene and acetylene derivatives.

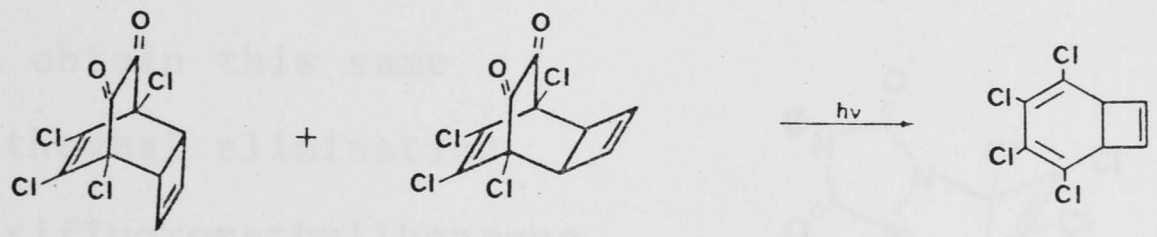
Woodward and Hoffmann, in exemplification of the principle of orbital-symmetry conservation, suggested that photochemical disrotatory opening of the cyclobutene ring in biCOTs should be an allowed process, leading to the opposite COT isomer (form A) to that formed in the thermal process (form B)[9].



Although no experiment specifically designed to test this proposal has been carried out, it may be significant that dimethyl cyclooctatetraene-1,8-dicarboxylate, prepared by the photochemical addition of dimethyl acetylenedicarboxylate to benzene[114], has been shown to exist exclusively in form A[122].

DISCUSSION

In the preceding Section, the formation of tetrachlorocyclohexadienes by photochemical elimination of the α-diketone bridge from adducts of tetrachloro-*o*-benzoquinone was described. Analogous bis-decarbonylation of *exo*- and *endo*-1,6,9,10-tetrachlorotricyclo[4.2.2.$0^{2,5}$]deca-3,9-dien-7,8-dione (115), prepared earlier as an aid in defining the stereochemistry of certain tetrachloro-*o*-benzoquinone adducts, was expected to yield 2,3,4,5-tetrachloro-biCOT (139).

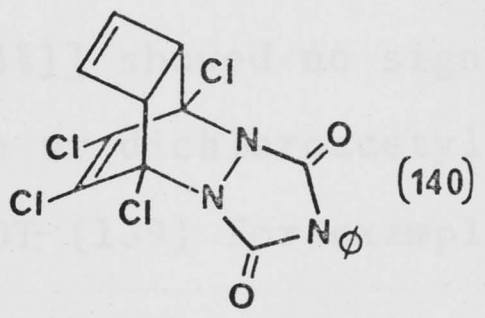


(115) (139)

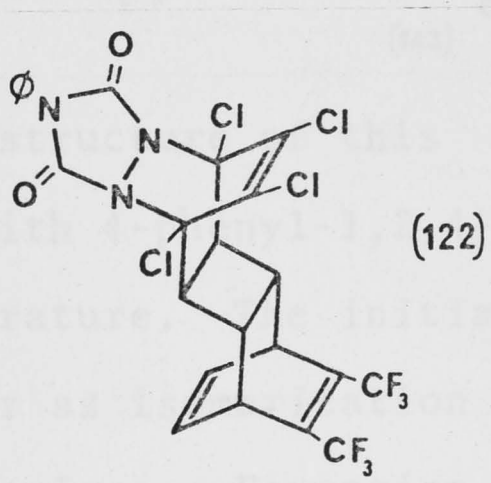
This proved to be the case. Irradiation (λ>300 nm) of the mixture of isomeric diketones was performed at 0° and monitored by p.m.r. spectroscopy. Gradual disappearance of the cyclobutyl protons of the diketones occurred (no difference in rate was observed), with concomitant gas evolution and formation of a single product, whose p.m.r. spectrum ($CDCl_3$) showed only two singlets of equal intensity at 6.26 and 3.94 δ. Preparative scale t.l.c. allowed isolation of this product in high (82%) yield, as a colourless crystalline solid, m.p. 38-39°. The p.m.r. spectrum suggested that the biCOT had indeed been formed, and this was confirmed by the u.v. spectrum [λ_{max} (EtOH) 286 (infl.), 296.5, 308, 321 (infl.) nm, ε 3700, 4600, 4250, 2100], which was quite characteristic

of the tetrachlorocyclohexadiene chromophore[104]. In the mass spectrum, besides successive losses of Cl [*m/e* 205 (base peak), 170 (97%)] from the molecular ion [*m/e* 240 (25%)], significant loss of acetylene to produce 1,2,3,4-tetrachlorobenzene (120) (*m/e* 214, 50%) was also consistent with the biCOT structure.

Further confirmatory evidence was derived from the rapid formation of an adduct (140) [p.m.r. ($CDCl_3$, δ p.p.m.): 7.47 (s, 5H, *N*-phenyl protons); 6.34 (s, 2H, $C_{3,4}$-olefinic protons); 3.75 (s, 2H, $C_{2,5}$-cyclobutyl protons); molecular ion *m/e* 415] on reaction with 4-phenyl-1,2,4-triazoline-3,5-dione (48) at room temperature. An attempt to obtain this same adduct by thermal elimination of *o*-bis(trifluoromethyl)benzene (50) from (122) failed because of excessive decomposition of the product.



(140)

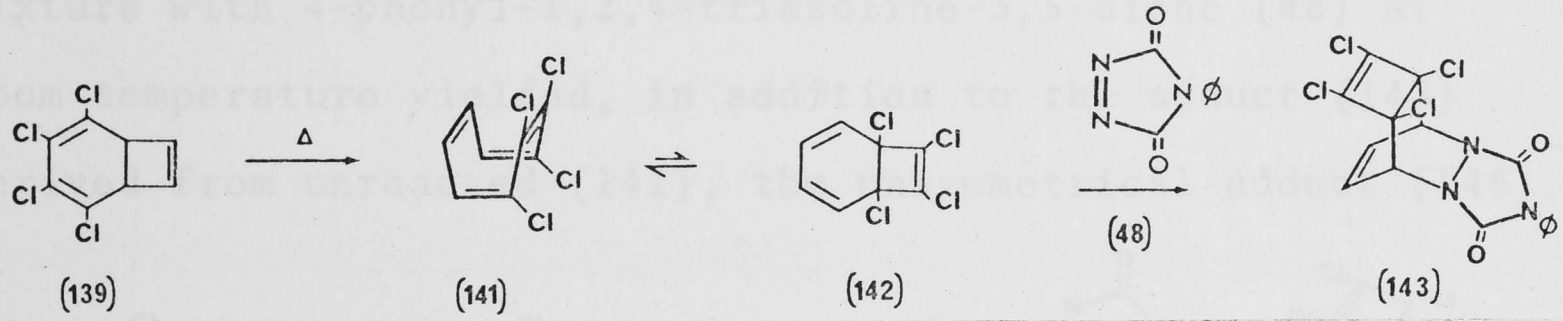


(122)

The biCOT (139) proved to be completely stable at room temperature. Warming in solution ($CDCl_3$) however, caused gradual transformation [$t_{\frac{1}{2}}$ (60°): 15 mins] to a different product, which was also obtained in the crystalline state (m.p. 55-57°).

That the new product was isomeric with the starting material was clearly indicated by analytical data, and by the mass spectrum (molecular ion *m/e* 240). Inspection of the u.v. spectrum [λ_{max} (EtOH) 237.5 nm, ε 4200, together with broad featureless absorption up to 350 nm] suggested that the product was a COT. The p.m.r. spectrum ($CDCl_3$),

which displayed two symmetrical multiplets of equal intensity centred at 6.32 and 6.14 δ, was consistent only with 1,2,3,8-tetrachloro-COT (141), since the alternative 1,2,3,4-tetra-substituted isomer would be expected to exhibit only a singlet in the p.m.r. spectrum. (This is in fact the case - *vide infra*). That the monocyclic COT structure could be distinguished from the isomeric biCOT was suggested by the mass spectral fragmentation, which besides successive losses of Cl [*m/e* 205 (98%), 170 (base peak), 135 (14%)] showed no significant loss of acetylene, chloroacetylene or dichloroacetylene [in contrast to 2,3,4,5-tetrachloro-biCOT (139) for example].



(139) (141) (142) (143)

Further evidence bearing on the structure of this product was derived from the reaction with 4-phenyl-1,2,4-triazoline-3,5-dione (48) at room temperature. The initial reaction was rapid, but then much slower as isomerization to 1,6,7,8-tetrachloro-biCOT (142) took place. Formation of the 2,3,4,5-tetrachloro adduct (143) was completely specific, consistent with the desire for maximum substitution in the cyclobutene ring in the formation of adducts derived from COTs[118]. The initial rapid reaction suggested that a small percentage of (142) was present in solutions of (141)*.

Exclusive formation of the single COT isomer from the biCOT (139), the result of a simple 6π disrotatory ring-

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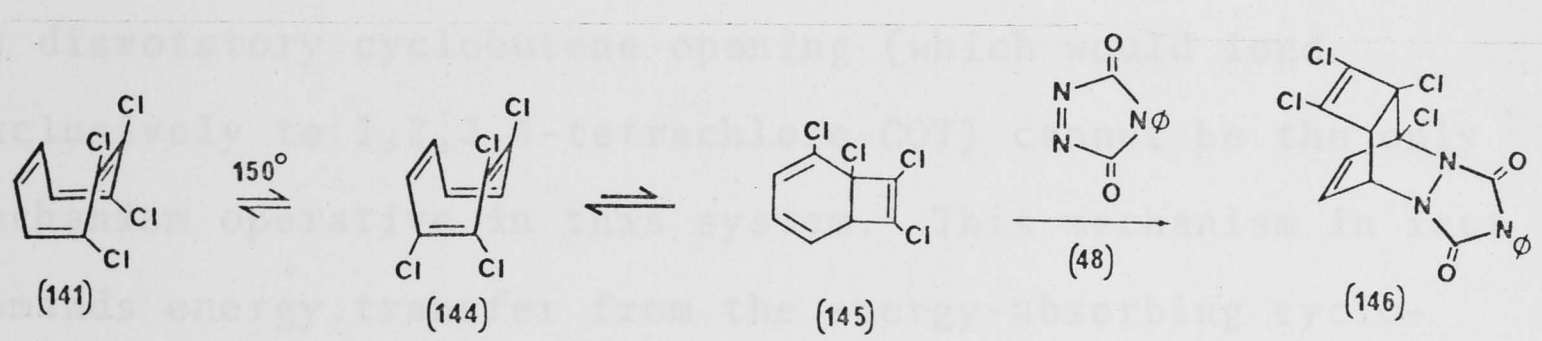
* The biCOT was not visible in p.m.r. spectra of (141), and hence cannot amount to more than 5%.

opening of the cyclohexadiene moiety, was in agreement with the predictions of Woodward and Hoffmann[9].

The COT (141) was stable up to 140°. Above this temperature slow conversion to another product occurred, 50% conversion being achieved after 4 hours at 150° (in deuteriochloroform solution). After 6 hours, an equilibrium was reached, containing 33% of the starting material. The product, which displayed only a sharp singlet at 6.23 δ in the p.m.r. spectrum ($CDCl_3$), was clearly 1,2,3,4-tetrachloro-COT (144), but isolation by t.l.c., g.l.c. or other means proved impossible. However, reaction of the equilibrium mixture with 4-phenyl-1,2,4-triazoline-3,5-dione (48) at room temperature yielded, in addition to the adduct (143) derived from unreacted (141), the unsymmetrical adduct (146).



The 1,2,3,4-tetrachloro isomer formed was that expected to result from isomerization of 1,2,3,4-tetrachloro-COT (144) to 1,2,7,8-tetrachloro-biCOT (145).

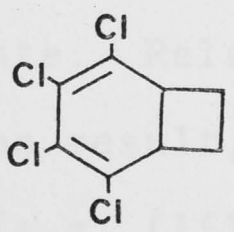
Interconversion of bond-fixed COTs has ample precedent both thermally[118] and photochemically[123], though the relatively high temperature required in the present case is indicative of a high activation energy. This is probably due to the reluctance of the four vicinal chlorine atoms to assume a coplanar orientation as required in the transition state for this process[118].

The stability of the biCOT (139) permitted direct study of its photochemistry, the irradiation (λ>300 nm) being carried out at 0°, well below the temperature required

for thermal degradation. Monitoring of the reaction by p.m.r. spectroscopy allowed the irradiation to be stopped after 20% conversion to photoproducts. Instead of photoaromatization however [no 1,2,3,4-tetrachlorobenzene (120) was detected] a 1:1 mixture of 1,2,3,8- and 1,2,3,4-tetrachloro-COTs [(141 and (144)] was produced. Control experiments in which 1,2,3,8-tetrachloro-COT (141) was irradiated under the same conditions, and for the same period of time, resulted in formation of a photostationary state containing 60% of the alternative COT isomer (144).

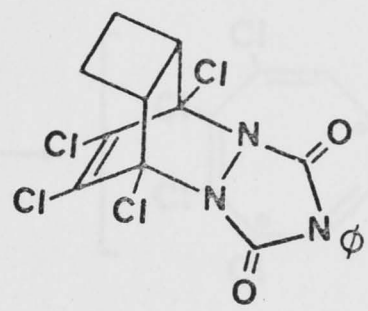
A concentration of 1,2,3,8-tetrachloro-COT in the biCOT photolysate higher than that in the photostationary state indicated that this product did not arise solely from the 1,2,3,4-tetrachloro isomer. Thus Woodward and Hoffmann's 4π disrotatory cyclobutene opening (which would lead exclusively to 1,2,3,4-tetrachloro-COT) cannot be the only mechanism operative in this system. This mechanism in fact demands energy transfer from the energy-absorbing cyclohexadiene chromophore to the cyclobutenyl double bond prior to ring-opening. Such a triplet energy transfer process was suggested in the previous Section, to account for the poor yield of photoaromatization products on photolysis of certain ring-fused tetrachlorocyclohexadienes.

In order to determine the extent of cyclobutenyl double bond participation in the photoreactions of the biCOT, the dihydro derivative (147) was prepared from the biCOT by Pd/C catalyzed hydrogenation. The structure of the product so obtained was unambiguously established by analysis and by the spectral data [λ_{max} 288



(147)

(infl.), 297.5, 307.5 (infl.), 323 (infl.) nm, ε 4050, 5100, 4150, 1850; p.m.r. ($CDCl_3$, δ p.p.m.): 3.58 (m, 2H, $C_{1,6}$-allylic cyclobutyl protons); 2.54 (m, 4H, $C_{7,8}$-cyclobutyl protons); molecular ion *m/e* 242]. Rapid formation of an adduct (148) with 4-phenyl-1,2,4-triazoline-3,5-dione (48) at room temperature also confirmed the diene structure.



(148)

Irradiation of this diene was carried out under conditions similar to those used for the biCOT, but even in this system, 1,2-photoaromatization to 1,2,3,4-tetrachlorobenzene (120) and ethylene was a minor reaction (22%).

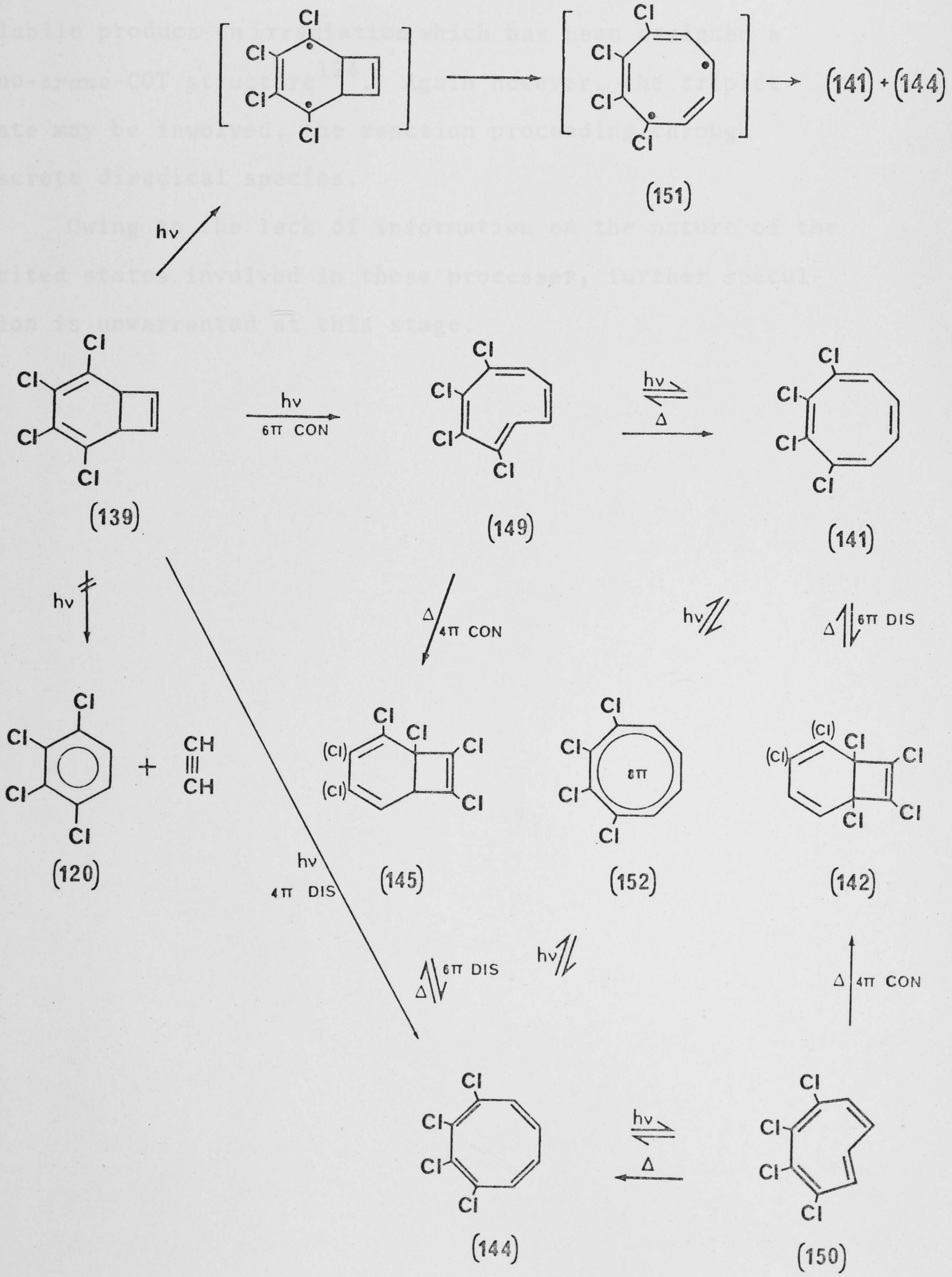
It is interesting to speculate on the mechanism of COT formation from the biCOT (139). Apart from the Woodward and Hoffmann mechanism discussed earlier, two mechanisms seem plausible (see Scheme 2).

1. Energy absorption by the tetrachlorocyclohexadiene chromophore may be followed by rapid 6π conrotatory ring-opening to produce the mono-*trans*-COT (149). COT (141) may then be formed directly by thermal or photochemical *cis-trans* isomerization, or COT (144) may arise from consecutive thermal 4π conrotatory ring-closure and 6π disrotatory ring-opening reactions.
2. Energy absorption may be followed by rapid inter-system crossing to the triplet state. Relaxation of orbital-symmetry control would then result, since de-excitation of a COT diradical [e.g. (151)] could lead to the formation of either COT isomer.

It is also interesting to speculate on the mechanism of interconversion of the COT isomers. Anet and Bock

SCHEME 2

Photochemical Isomerization of the BiCOT (139)



suggested that a planar (anti-aromatic?) transition state [e.g. (152)] may be involved[123]. However, mechanisms may be written involving mono-*trans*-COTs [e.g. (149) and (150)]. Although no evidence of such intermediates was found in the present case, 1,2,4,7-tetraphenyl-COT has been shown to yield a labile product on irradiation which has been assigned a mono-*trans*-COT structure[124]. Again however, the triplet state may be involved, the reaction proceeding through discrete diradical species.

Owing to the lack of information on the nature of the excited states involved in these processes, further speculation is unwarranted at this stage.

EXPERIMENTAL SECTION

Unless otherwise stated, all u.v. spectra were recorded in 90% ethanol solution on a Unicam SP 800 spectrophotometer. I.r. spectra were recorded on a Unicam SP 200G instrument, either in nujol mulls, carbon tetrachloride solution (0.1 mm sodium chloride cells) or in the vapour phase (10 cm cell with sodium chloride windows). Proton and ^{19}F n.m.r. spectra were recorded at 60 and 56.458 MHz respectively, on a Perkin-Elmer R 10 instrument using internal tetramethylsilane and external trifluoroacetic acid as references. Low resolution mass spectra were recorded on A.E.I. MS-902 and Varian MAT CH 7 spectrometers, the former also being used for high resolution spectra and the latter, in combination with a Varian Aerograph Series 1400 chromatograph, also being used for combined g.l.c. - mass spectrometric analyses. For other g.l.c. work, a Hewlett Packard Series 5750 instrument was employed. All preparative scale t.l.c. was carried out on 20 x 20 or 20 x 60 cm glass plates, using silica gel (Merck $HF_{254 + 366}$) as adsorbent.

Microanalyses were performed by the Australian Microanalytical Service, Melbourne, under the direction of Dr. R.D. McDonald or by the A.N.U. Microanalytical Service under the direction of Miss B. Stevenson and Dr. J.E. Fildes. All melting points were determined on a Gallenkamp melting point apparatus and are uncorrected.

For photolyses, an American Hanovia (AH) medium-pressure mercury lamp (450 watt) was inserted into a filter sleeve of vycor, corex or pyrex glass and placed inside a water-cooled quartz probe. Solutions of 100 ml or more were irradiated in a pyrex reaction vessel into which the probe

assembly could be fitted, while stirring was achieved by means of a gas-lift circulator (dry oxygen-free nitrogen normally being used). For volumes of 20 ml or less, a quartz tube containing the sample was directly attached to the outside surface of the probe assembly. In some instances, careful monitoring of the reaction by p.m.r. spectroscopy was desirable. In such cases, a quartz tube of 0.5 ml capacity was used (a quartz n.m.r. tube was also occasionally used). For volumes of *ca.* 0.1 ml, a very thin quartz tube was used, which could be directly inserted into an n.m.r. tube. P.m.r. spectra recorded in this way were quite satisfactory, provided excessive polymer formation did not occur.

cis-3,4-Dichlorocyclobutene

Redistilled cyclooctatetraene (80.3 g, 0.8 mole) in anhydrous carbon tetrachloride (160 ml) was cooled to *ca.* -30° in an acetone/dry ice bath and vigorously stirred while chlorine gas (56.8 g, 0.8 mole, purified by passage through potassium permanganate solution and dilute and concentrated sulphuric acids, and dried over calcium chloride) was slowly passed in.

The resulting light yellow solution was shaken with anhydrous potassium carbonate (80 g) to remove the hydrogen chloride formed, and was then filtered directly into a flask containing redistilled dimethyl acetylenedicarboxylate (108.0 g, 0.76 mole) in carbon tetrachloride (100 ml). After refluxing for 4 hours, the solvent and volatile impurities were removed by evacuating at 80°/0.05 mm for 2 hours.

The syrupy residue was then slowly added to a magnetically stirred flask heated in an oil bath at 190-200° and maintained at a pressure of 65 mm. The fraction (115 g) distilling at 100-140° was collected in a receiver cooled to -78° in an acetone/dry ice bath.

This material was then fractionated through a 2½ x 20 cm Hempel column packed with glass helices. *cis*-3,4-Dichlorocyclobutene (36.7 g, 37%) was collected at 74-78°/54 mm (lit.[125] 74°/60 mm) as a colourless oil which crystallized on storing at 0° overnight.

P.m.r. ($CDCl_3$, δ p.p.m.) 6.31 (m, 2H, $C_{1,2}$-olefinic protons); 5.20 (m, 2H, $C_{3,4}$-cyclobutyl protons).

Cyclobutadieneiron Tricarbonyl

To a mechanically stirred solution of *cis*-3,4-dichlorocyclobutene (6.15 g, 0.05 mole) and

bromoform* (0.6 g) in refluxing *n*-pentane (60 ml, dried and redistilled from P_2O_5) under dry oxygen-free nitrogen was added diiron nonacarbonyl (Alfa, 55 g, 0.15 mole) in 4 portions over 4 hours. Carbon monoxide evolution had then ceased and the dark brown reaction mixture was filtered through cellulose powder, the filter being thoroughly washed with *n*-pentane†. Evaporation of the solvent at room temperature under reduced pressure left a dark green liquid, which was then distilled. After a forerun (13.6 g, b.p. up to 40°/8 mm) consisting chiefly of iron pentacarbonyl, the product (4.60 g, 48%) was collected at 53-55°/4 mm (lit.[126] 47-48°/3 mm) as a light green oil,# which crystallized on cooling.

P.m.r. ($CDCl_3$, δ p.p.m.) 3.99 (s).

Hexakis(trifluoromethyl)benzene (35)

Hexafluorobut-2-yne (14.6 g, 0.09 mole) was sealed into a previously evacuated (*ca.* 10^{-3} mm) heavy-wall pyrex tube (450 ml capacity) and heated in a furnace at 380° for 60 hours. After cooling, the brown crystalline solid was washed out with acetone, and the solvent evaporated.

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* Purified by washing with water, drying over anhydrous magnesium sulphate, and fractional distillation.

† 13 g of unreacted diiron nonacarbonyl was recovered from the filter by liberal washing of the collected material with 25% hydrochloric acid, water, ethanol, and finally ether under nitrogen (c.f. ref.[127]).

\# The green colouration is due to a higher-boiling impurity. However, this appeared to have no adverse effect on the subsequent oxidative generation of cyclobutadiene (*vide infra*).

Sublimation (80°/0.05 mm) and recrystallization from carbon tetrachloride yielded the product (9.50 g, 65%) as fine colourless plates, m.p. (sealed tube) 204-206° (lit.[39] 209°).

λ_{max} ($CHCl_3$) 285 nm, ε 140.

ν_{max} 729 s, 751 m, 807 w, 1054 s, 1150-1260 vs cm^{-1}.

^{19}F n.m.r. (Acetone) 25.4 δ (s).

m/e 486 (Molecular ion, 86%), 467 (96%), 417 (base peak), 398 (56%), 379 (58%), 367 (78%), 348 (74%), 329 (66%), 279 (63%), 210 (32%), 141 (26%), 69 (65%).

Hexakis(trifluoromethyl)benzvalene (36)

Hexakis(trifluoromethyl)benzene (35) (7.29 g, 0.015 mole) was dissolved in acetone (20 ml) in a quartz tube and irradiated at room temperature (AH lamp, vycor filter) for 16 hours. A ^{19}F n.m.r. spectrum revealed that *ca.* 32% conversion to the benzvalene (36) had occurred, while no other products were detectable.

The acetone was removed by fractional distillation (1 x 5 cm Hempel column packed with glass helices) at atmospheric pressure. Distillation of the residue at room temperature under reduced pressure (0.05 mm) yielded the benzvalene, which was collected in an acetone/dry ice-cooled trap. Sublimation of the solid residue at 80° (0.05 mm) allowed recovery of the unreacted benzene (4.35 g).

The product, a colourless liquid (2.62 g, 89% calculated from unrecovered benzene), was suitable for use in the subsequent reactions.

ν_{max} (liquid film) 725 w, 882 w, 1051 m, 1215 vs (broad), 1275 s, 1346 s, 1663 m cm^{-1}.

^{19}F n.m.r. (Neat, δ p.p.m.) (see page 16) 21.5 (septet (J=5.6 Hz), 6F, $C_{1,6}$-bicyclobutyl CF_3 groups); 18.7 (m, 6F, $C_{3,4}$-olefinic CF_3 groups); 15.0 (m, 6F,

$C_{2,5}$-allylic CF_3 groups).

m/e 486 (Molecular ion, 17%), 467 (89%), 417 (base peak), 69 (58%).

endo-1,6,7,8,9,10-Hexakis(trifluoromethyl)pentacyclo-[4.4.0.$1^{2,5}$.$0^{7,9}$.$0^{8,10}$]undec-3-ene (39)

Cyclopentadiene (33 mg, 0.5 mmole, freshly prepared from the dimer) was added to an n.m.r. tube containing hexakis(trifluoromethyl)benzvalene (36) (243 mg, 0.5 mmole) in acetone-d_6 (0.3 ml). A p.m.r. spectrum showed that reaction was complete within a few minutes. The solvent was removed at room temperature under reduced pressure, and the residual white solid sublimed (room temperature, 0.05 mm). The product (197 mg, 71%) was obtained as colourless prisms, m.p.* (sealed tube) *ca.* 250°, with decomposition (Found: C, 36.6; H, 1.1; F, 62.2. $C_{17}H_6F_{18}$ requires C, 37.0; H, 1.1; F, 61.9%).

The u.v. spectrum showed end absorption only.

ν_{max} 668 ms, 736 ms, 759 ms, 820 ms, 868 m, 1060 m, 1071 m, 1150-1330 vs (broad) cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 6.48 (m, 2H, $C_{3,4}$-olefinic protons); 3.43 (m, 2H, $C_{2,5}$-bridgehead protons); 2.7-1.8 (m, 2H, C_{11}-methylene protons).

^{19}F n.m.r. (Acetone, δ p.p.m.) (see page 16) 24.2 (m, 3F, C_8-bicyclobutyl CF_3 group); 20.8 (m, 3F, C_9-bicyclobutyl CF_3 group); 15.7 (m, 6F, $C_{7,10}$-cyclopropyl CF_3 groups); 15.5 (m, 6F, $C_{1,6}$-CF_3 groups).

m/e 552 (Molecular ion, 63%), 533 (base peak), 483

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* Melting points of these fluorohydrocarbons were extremely difficult to determine on account of their very high volatility.

(67%), 202 (78%), 69 (47%), 66 (91%).

Attempted Reaction of Hexakis(trifluoromethyl)benzvalene (36) with:

(a) 2,5-Dimethyl-3,4-diphenylcyclopenta-2,4-dienone (40)

The cyclopentadienone dimer (130 mg, 0.25 mmole) and the benzvalene (243 mg, 0.5 mmole) were heated under reflux in benzene (4 ml) for 4 days. After evaporation under reduced pressure, a p.m.r. spectrum of the residue showed that no reaction had taken place.

Similarly, no reaction was observed after refluxing in benzotrifluoride (b.p. 103°) for 8 days.

(b) Dimethyl Tetrachlorocyclopentadiene Acetal (41)

The dimethyl acetal (26.4 mg, 0.1 mmole), the benzvalene (48.6 mg, 0.1 mmole) and carbon tetrachloride (0.5 ml) were sealed into an n.m.r. tube and heated at temperatures up to 150° for 18 hours. Again, p.m.r. spectra showed that no reaction had taken place.

(c) α-Pyrone (42)

Freshly redistilled α-pyrone (32 mg, 0.33 mmole), the benzvalene (162 mg, 0.33 mmole) and deuteriochloroform (0.5 ml) were sealed into an n.m.r. tube and heated at temperatures up to 150° for 10 hours. P.m.r. spectra showed that no reaction had occurred.

(d) Butadiene

The benzvalene (162 mg, 0.33 mmole) in deuterio-dimethylsulphoxide (1.0 ml) was heated in an oil bath at 100° while butadiene gas was slowly passed through during 3 hours. A p.m.r. spectrum showed no reaction had occurred.

syn- and *anti*- 1,2,3,4,5,6-Hexakis(trifluoromethyl)pentacyclo[4.4.0.$0^{2,4}$.$0^{3,5}$.$0^{7,10}$]dec-8-ene (43) and (44)

A mixture of cyclobutadieneiron tricarbonyl (192 mg, 1 mmole) and hexakis(trifluoromethyl)benzvalene (36) (486 mg, 1 mmole) in 95% ethanol (25 ml) was cooled to 0° in an ice bath and stirred vigorously while powdered ceric ammonium nitrate (4 g) was added during 5 minutes.

After stirring for an additional 15 minutes, the dark red reaction mixture was poured into cold water (100 ml) and extracted with chloroform (3 x 50 ml). After washing the extracts with water (3 x 50 ml), and drying over anhydrous magnesium sulphate, the solvent was removed by evaporation below room temperature. Sublimation of the residue at room temperature (0.05 mm) gave a colourless waxy crystalline *solid* (280 mg, 52%) m.p.* (sealed tube) *ca.* 180° (Found: C, 35.45; H, 0.9; F, 63.4. $C_{16}H_4F_{18}$ requires C, 35.7; H, 0.75; F, 63.5%).

G.l.c. (6' x 3/8" column of 10% SE30 on Embacel, 70°) allowed separation of the *syn* isomer (retention time 5.6 mins) and the *anti* isomer (retention time 6.9 mins). (No separation was detected following t.l.c. or partial sublimation).

Both isomers showed end absorption only in the u.v. spectrum.

syn isomer (43)

ν_{max} 720 m, 745 m, 784 m, 796 m, 875 m, 1077 ms, 1150-1380 vs cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 6.40 (m, 2H, $C_{8,9}$-olefinic protons); 3.60 (m, 2H, $C_{7,10}$-cyclobutyl protons).

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* See footnote page 80.

^{19}F n.m.r. (Acetone, δ p.p.m.) (see page 19) 25.0 (m, 3F, C_3-bicyclobutyl CF_3 group); 21.5 (m, 3F, C_4-bicyclobutyl CF_3 group); 16.25 (m, 6F, $C_{2,5}$-cyclopropyl CF_3 groups); 12.9 (m, 6F, $C_{1,6}$-CF_3 groups).

m/e 538.0023 (Molecular ion, 2%, $C_{16}H_4F_{18}$ requires 538.0025), 499 (4%), 469 (4%), 324 (19%), 255 (34%), 214 (28%), 195 (17%), 145 (23%), 69 (base peak).

anti isomer (44)

ν_{max} 741 mw, 806 m, 895 mw, 1073 m, 1150-1380 vs cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 6.40 (m, 2H, $C_{8,9}$-olefinic protons); 3.75 (t (J=1.3 Hz), 2H, $C_{7,10}$-cyclobutyl protons).

^{19}F n.m.r. (Acetone, δ p.p.m.) (see page 19) 23.5 (m, 3F, C_3-bicyclobutyl CF_3 group); 21.5 (m, 3F, C_4-bicyclobutyl CF_3 group); 15.4 (m, 6F,$C_{2,5}$-cyclopropyl CF_3 groups); 9.4 (m, 6F, $C_{1,6}$-CF_3 groups).

m/e 538.0023 (Molecular ion, $C_{16}H_4F_{18}$ requires 538.0025).

The low resolution mass spectrum of the *anti* isomer was identical to that of the *syn* isomer (*vide supra*).

1,2,3,4,5,6-Hexakis(trifluoromethyl)tetracyclo-[4.4.0.$0^{2,4}$.$0^{3,5}$]deca-7,9-diene (47)

A mixture of *syn*- and *anti*-1,2,3,4,5,6-hexakis(trifluoromethyl)pentacyclo[4.4.0.$0^{2,4}$.$0^{3,5}$.$0^{7,10}$]dec-8-ene (43) and (44) (215 mg, 0.4 mmole) was sealed into a small glass tube (approximate capacity 1 ml) and heated in a Wood's Metal bath at 240° for 1 hour. G.l.c. analysis (6' x 3/8" column of 10% SE30 on Embacel, 70°) of the product showed that less than 2% of the starting material remained. Sublimation (50°/0.05 mm) gave the *diene* (178 mg, 83%) as a colourless waxy crystalline solid. An analytical sample was obtained by g.l.c. (*vide supra*, retention time 8.8 mins) (Found: C, 35.6; H, 0.8; F, 63.2.

$C_{16}H_4F_{18}$ requires C, 35.7; H, 0.75; F, 63.5%).

λ_{max} 251, 258, 268 nm, ε 4350, 4400, 2500.

ν_{max} 732 ms, 860 ms, 1008 m, 1073 ms, 1205 vs, 1230 vs, 1247 vs, 1270 s, 1315 s, 1350 s cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 6.6-6.3 (m, 2H, $C_{8,9}$-olefinic protons); 6.3-5.9 (m, 2H, $C_{7,10}$-olefinic protons).

^{19}F n.m.r. ($CHCl_3$, δ p.p.m.) 23.4 (m, 3F, C_3-bicyclobutyl CF_3 group); 22.1 (m, 3F, C_4-bicyclobutyl CF_3 group); 17.1 (m, 6F, $C_{2,5}$-cyclopropyl CF_3 groups); 10.5 (m, 6F, $C_{1,6}$-CF_3 groups).

m/e 538 (31%), 519 (10%), 500 (57%), 469 (25%), 450 (43%), 400 (10%), 381 (52%), 324 (59%), 305 (32%), 255 (66%), 236 (26%), 214 (54%), 195 (39%), 145 (43%), 69 (base peak).

Adduct (49) of 1,2,3,4,5,6-Hexakis(trifluoromethyl)tetracyclo-[4.4.0.$0^{2,4}$.$0^{3,5}$]deca-7,9-diene (47) and 4-phenyl-1,2,4-triazoline-3,5-dione (48)

A solution of the diene (108 mg, 0.2 mmole) and excess triazolinedione in chloroform (2 ml) was set aside for 24 hours at room temperature. Preparative scale t.l.c. (silica/chloroform) allowed separation of the *adduct* (91 mg, 84%) from unreacted diene* (30 mg). The adduct crystallized from ethanol as colourless prisms m.p. 195-196° (Found: C, 40.4; H, 1.4; N, 6.1; F, 47.8. $C_{24}H_9N_3F_{18}O_2$ requires C, 40.4; H, 1.3; N, 5.9; F, 47.95%).

λ_{max} 256 nm, ε 3400.

ν_{max} 801 m, 1079 m, 1209 s, 1236 s, 1270 s, 1413 m,

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* Confirmed by comparison of g.l.c. retention time, and p.m.r. and u.v. spectra with that of the starting material.

1508 m, 1727 s, 1749 m, 1795 m cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.50 (s, 5H, *N*-phenyl protons); 6.69 (dd, 2H, $C_{11,12}$-vinylic protons); 5.71 (dd, 2H, $C_{2,5}$-bridgehead protons).

^{19}F n.m.r. ($CHCl_3$, δ p.p.m.) 24.2 (m, 3F, C_8-bicyclobutyl CF_3 group); 20.7 (m, 3F, C_9-bicyclobutyl CF_3 group); 16.2 (m, 6F, $C_{7,10}$-cyclopropyl CF_3 groups); 15.8 (m,.6F, $C_{1,6}$-CF_3 groups).

m/e 713 (Molecular ion, 24%), 575 (10%), 227 (base peak), 119 (30%), 80 (45%).

Irradiation of 1,2,3,4,5,6-Hexakis(trifluoromethyl)tetracyclo[4.4.0.$0^{2,4}$.$0^{3,5}$]deca-7,9-diene (47)

The diene (10 mg) was dissolved in ether (0.1 ml) in a thin quartz tube and irradiated at 0° (AH lamp, vycor filter), while the course of the reaction was monitored by g.l.c. (SE30 on Embacel, 70°). The reaction was complete after 6 hours.

The products, *syn*- and *anti*-1,2,3,4,5,6-hexakis(trifluoromethyl)pentacyclo[4.4.0.$0^{2,4}$.$0^{3,5}$.$0^{7,10}$]dec-8-ene (43) and (44), were present in equal proportion (43.3 and 43.4% respectively), and were identified by comparison of g.l.c. retention times and i.r. spectra with authentic samples (*vide supra*). A third product (13.3%, retention time 7.6 mins) could not be identified. *o*-Bis(trifluoromethyl)benzene (50) (retention time 2.5 mins) was not present in the photolysate (limit of detectability *ca.*1%).

Pyrolysis of 1,2,3,4,5,6-Hexakis(trifluoromethyl)tetracyclo[4.4.0.$0^{2,4}$.$0^{3,5}$]deca-7,9-diene (47)

(a) 340°

A small sample (*ca.* 5 mg) of the tetracyclodecadiene was sealed into a small glass tube (approximate volume 1 ml)

and immersed in a Wood's Metal bath at 340° for 2 minutes. G.l.c. analysis (6' x 3/8" column of 10% SE30 on Embacel, 70°) of the product revealed that only one compound was present, whose retention time and u.v. spectrum were identical to that of the starting material.

(b) Flash Vacuum Pyrolysis, 700°

The flash vacuum pyrolysis apparatus was described in the text (see page 24). The flask containing the diene (2-250 mg) was cooled in liquid nitrogen until a satisfactory vacuum (0.001 mm) was established, then warmed to 50° to allow slow sublimation of the contents through the pyrolysis tube. The pyrolysis products were collected in a trap cooled in liquid nitrogen, which was then sealed off by means of two taps. The contents could be transferred in vacuum to an n.m.r. tube for recording of p.m.r. and ^{19}F n.m.r. spectra, or to a tap vessel* for g.l.c. - mass spectral analysis. All this data is included in the text, except for the complete mass spectra of the butatriene (57) [*m/e* 324 (molecular ion, 40%), 305 (91%), 255 (base peak), 236 (56%), 205 (51%)], the $C_4(CF_3)_6$ product (53) [*m/e* 462 (molecular ion, 9%), 443 (17%), 393 (12%), 374 (35%), 355 (81%), 305 (74%), 286 (58%), 267 (75%), 255 (90%), 236 (base peak), 217 (89%), 205 (58%), 167 (46%)], and the $C_8(CF_3)_8$ product (54) [*m/e* 648 (molecular ion, 3%), 628 (base peak), 579 (82%), 541 (45%), 490 (55%), 421 (45%)].

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* This vessel was fitted with a rubber septum, through which it could be charged with helium to atmospheric pressure for withdrawal of gas samples.

To the n.m.r. tube containing the crude pyrolysate was added an excess of freshly redistilled cyclopentadiene. Reaction with hexafluorobut-2-yne produced 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (52), which was identified by g.l.c. and spectral comparison with an authentic sample (*vide infra*). The second 1:1 *adduct* (59) was separated by preparative scale g.l.c. (retention time on a 6' x 3/8" column of 10% SE30 on Embacel at 80°: 5.2 mins) as a colourless liquid.

λ_{max} 234, 279 (infl.), ε *ca.* 2000, 700.

ν_{max} (CCl_4) 694 w, 723 w, 1144 m, 1192 vs, 1208 vs, 1258 vs, 1282 s, 1334 m, 1640 w, 1678 w, 2894 w, 2964 w, 3007 w cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 6.96 (t, 2H, olefinic protons); 3.80 (m, 2H, bridgehead protons); 2.40 (m, 2H, methylene protons).

^{19}F n.m.r. ($CHCl_3$, δ p.p.m.) 13.5 (m, 6F), 13.1 (m, 6F).

m/e 390.0273 (Molecular ion, 13%, $C_{13}H_6F_{12}$ requires 390.0278), 371 (13%), 321 (40%), 69 (20%), 66 (base peak).

o-Bis(trifluoromethyl)benzene (50)

Redistilled cyclohexadiene (1.60 g, 0.02 mole) and hexafluorobut-2-yne (3.24 g, 0.02 mole) were sealed into an evacuated 75 ml heavy-wall pyrex tube, and carefully heated at 200° for 1 hour. After cooling, the tube was opened and the product distilled in vacuum, yielding the benzene (3.55 g, 83%) as a colourless liquid, b.p. 141-143° (lit.[128] 143°).

The retention time on a 3' x 1/8" column of 5% SE30 on Varaport 30 at 35° was 3.6 mins.

λ_{max} 257, 260 (infl.), 262, 266 (infl.), 269.5 nm, ε 610, 680, 825, 600, 750.

ν_{max} (vapour phase) 783 m, 1050 m, 1199 s, 1287 m, 1325 s cm^{-1}.

The p.m.r. spectrum ($CDCl_3$) showed only a symmetrical multiplet (AA'BB') centred at 7.82 δ.

^{19}F n.m.r. ($CHCl_3$) 19.5 δ (s).

m/e 214 (Molecular ion and base peak), 195 (65%), 164 (23%), 145 (91%), 69 (9%).

2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (52)

Freshly redistilled cyclopentadiene (0.66 g, 0.01 mole) in a small tared flask was cooled in a liquid nitrogen bath while hexafluorobut-2-yne was slowly passed in. After warming to room temperature, the flask was weighed, and this procedure was repeated until the increase in weight was 1.62 g (0.01 mole). Distillation in vacuum then gave the bicycloheptadiene (2.03 g, 89%) as a colourless liquid.

The retention time on a 3' x 1/8" column of 5% SE30 on Varaport 30 at 35° was 2.5 mins.

λ_{max} 244 nm, ε 140.

ν_{max} (vapour phase) 734 w, 1168 s, 1202 ms, 1311 s, 1362 m, 1691 w cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.04 (t (J=*ca.* 3 Hz), 2H, $C_{5,6}$-olefinic protons); 3.98 (m, 2H, $C_{1,4}$-bridgehead protons); 2.23 (m (AB, J_{AB}=*ca.* 7 Hz), 2H, C_7-methylene protons).

^{19}F n.m.r. ($CHCl_3$) 14.6 δ (s).

m/e 228 (Molecular ion, 31%), 202 (22%), 189 (14%), 159 (base peak), 109 (21%), 69 (8%), 66 (21%).

Cyclohexa-3,5-diene-*trans*-1,2-dicarboxylic Acid

A mixture of phthalic acid (41.5 g, 0.25 mole) and powdered anhydrous sodium acetate (41.0 g, 0.5 mole) in water (400 ml) was stirred vigorously, with cooling, while

sodium amalgam (5%, 575 g, 1.25 mole sodium) and 50% aqueous acetic acid (160 ml) were added at such a rate as to maintain the temperature in the range 8-12° and the pH at 6. Stirring was continued until all the sodium amalgam had reacted (total time 10 hours).

After filtering, the solution was acidified with cold 20% sulphuric acid to pH 2, yielding the crude diacid (33.5 g, 80%), which was suitable for conversion to the anhydride.

Cyclohexa-3,5-diene-*cis*-1,2-dicarboxylic Anhydride

The diacid (33.5 g, 0.2 mole) was placed in a 3-necked 250 ml flask in an oil-bath at 100-105°, and after flushing with dry nitrogen, acetic anhydride (125 ml) was added with vigorous stirring. The diacid dissolved in 8 minutes, and after an additional 2 minutes, stirring was discontinued and the flask cooled. The solvent was evaporated in vacuum below 45°, residual acetic anhydride being removed by azeotropic distillation with xylene in vacuum.

The crystalline residue was sublimed (60°/0.05 mm) to give the *cis*-anhydride (24.9 g, 83%). Recrystallization from carbon tetrachloride gave colourless prisms, m.p. 108-109° (lit.[64] 108-109.5°).

λ_{max} 256, 264 nm, ε 4800, 4600.

ν_{max} 1760 s, 1842 s cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 6.3-5.7 (m, 4H, $C_{3,4,5,6}$-olefinic protons); 4.02 (m, 2H, $C_{1,2}$-protons).

m/e 150 (Molecular ion, 33%), 106 (22%), 78 (base peak).

anti-Bicyclo[2.2.0]hex-5-ene-*cis*-2,3-dicarboxylic Anhydride (78)

Cyclohexa-3,5-diene-*cis*-1,2-dicarboxylic anhydride (3.0 g, 0.02 mole) was dissolved in ether (900 ml, dried

and redistilled over sodium) and irradiated at 0° (AH lamp, quartz probe, vycor filter). Care was taken to exclude oxygen from the reaction vessel. Argon or nitrogen for use in a gas-lift circulator was passed over a cuprous oxide deoxygenator, anhydrous calcium chloride and potassium hydroxide pellets before pre-saturation with ether to minimize evaporation. A yellow polymeric deposit was occasionally removed from the quartz probe, and the course of the irradiation was followed by observing the disappearance of the diene absorption (at 256 nm) in the u.v. spectrum. The solution was evaporated to dryness, and the p.m.r. spectrum checked to ensure that no starting material remained.

The crude photolysate was then transferred to a Soxhlet thimble and extracted with *n*-hexane. The extracts were evaporated, and sublimed (80°/0.05 mm) to give the crude product (240 mg, 8%). Recrystallization from ether gave colourless prisms, m.p. 160-162° (lit.[64] 160-164°).

The u.v. spectrum showed end absorption only.

ν_{max} 755 m, 1770 s, 1845 m cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 6.47 (m, 2H, $C_{5,6}$-olefinic protons); 3.70 (m, 2H, $C_{1,4}$-cyclobutyl protons); 3.41 (m, 2H, $C_{2,3}$-cyclobutyl protons).

2,5-Dimethyl-3,4-diphenyltetracyclo[4.4.0.$1^{2,5}$.$0^{7,10}$]undec-3-en-11-one-*cis*-8,9-dicarboxylic Anhydride (79)

anti-Bicyclo[2.2.0]hex-5-ene-*cis*-2,3-dicarboxylic anhydride (78) (150 mg, 1 mmole), 2,5-dimethyl-3,4-diphenyl-cyclopenta-2,4-dienone dimer (260 mg, 0.5 mmole) and benzene (5 ml) were heated together under reflux for 3 hours. The solution was evaporated to dryness, and the residue triturated with ether/*n*-hexane to give the *adduct* (303 mg, 74%). Recrystallization from benzene/*n*-hexane gave

colourless crystals, m.p. 245-246° (Found: C, 79.1; H, 5.6; O, 16.0. $C_{27}H_{22}O_4$ requires C, 79.0; H, 5.4; O, 15.6%).

λ_{max} 247, 262 nm, ε 9000, 9900.

ν_{max} 700 ms, 918 ms, 1071 ms, 1247 ms, 1775 s, 1864 m cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.3-6.8 (m, 10H, aromatic protons); 3.55 (broad s, 2H, $C_{8,9}$-cyclobutyl protons); 2.84 (broad s, 2H, $C_{1,6}$-cyclobutyl protons); 2.76 (broad s, 2H, $C_{7,10}$-cyclobutyl protons); 1.21 (s, 6H, $C_{2,5}$-methyl protons).

m/e 410 (Molecular ion, 1%), 382 (14%), 258 (base peak).

Photolysis of 2,5-Dimethyl-3,4-diphenyltetracyclo-[4.4.0.$1^{2,5}$.$0^{7,10}$]undec-3-en-11-one-*cis*-8,9-dicarboxylic Anhydride (79)

The ketone (75 mg, 0.183 mmole) was suspended in acetone-d_6 (0.5 ml) in a thin quartz tube and irradiated at 0° (AH lamp, vycor filter). Periodic p.m.r. spectra showed that almost complete conversion to photoproducts had occurred after 10 hours.

The solvent was removed by sublimation at room temperature and atmospheric pressure onto a cold finger at -78°. Sublimation of the residue at 30° (0.05 mm) gave cyclobut-3-ene-*cis*-1,2-dicarboxylic anhydride (81) (7 mg, 30%*), m.p. 87-88° (lit.[129] 90°).

ν_{max} 685 s, 731 s, 855 s, 910 s, 1070 s, 1200 s, 1750 s, 1850 w cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 6.51 (broad s, 2H, $C_{3,4}$-

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* This rather poor isolated yield was due to the difficulty of recovering the very small quantity of (81) present in the photolysis mixture.

olefinic protons); 4.05 (broad s, 2H, $C_{1,2}$-allylic cyclobutyl protons).

m/e 124 (Molecular ion, 0.5%), 80 (22%), 52 (base peak).

1,2-Dimethoxycarbonyl-1,2-diazacyclohex-4-ene (85)

Dimethyl azodicarboxylate* (14.6 g, 0.1 mole) and benzene (10 ml) were heated under reflux while butadiene gas was slowly passed through. After 2-3 hours, the solution became light yellow, and the product (16.6 g, 83%) was isolated by distillation as a colourless oil, b.p. 102-104°/1 mm, which slowly crystallized. The m.p. was 36-38° (lit.[66] 38°).

P.m.r. ($CDCl_3$, δ p.p.m.) 5.87 (m, 2H, $C_{4,5}$-olefinic protons); 4.4-4.0 (m, 4H, $C_{3,6}$-allylic protons); 3.80 (s, 6H, *O*-methyl protons).

1,2-Dimethoxycarbonyl-1,2-diazacyclohexa-3,5-diene (86)†

1,2-Dimethoxycarbonyl-1,2-diazacyclohex-4-ene (85) (5.0 g, 0.025 mole), *N*-bromosuccinimide (5.10 g, 0.03 mole) and benzoyl peroxide (0.1 g) were refluxed together in carbon tetrachloride (1 litre) for 2½ hours, when all the *N*-bromosuccinimide had reacted. The cooled reaction mixture was then evaporated under reduced pressure to a volume of 125 ml, filtered, and evaporated to dryness.

The residual allylic bromide was dissolved in dry

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* Prepared by reaction of hydrazine hydrate with methyl chloroformate, followed by oxidation of the resulting dimethyl hydrazinodicarboxylate with chlorine (c.f. ref.[130]).

† Details of this procedure were kindly supplied by Prof. L.J. Altman of Stanford University, California.

toluene (100 ml), and brought to the boiling point, when 2,6-lutidine (2.7 g, 0.025 mole, redistilled from sodium aluminium hydride) was immediately added. After refluxing for 5 minutes, the solution was rapidly cooled in an ice bath. Lutidine hydrobromide was removed by washing with 5% hydrochloric acid (3 x 50 ml). After further washing with aqueous sodium bicarbonate (50 ml) and water (3 x 50 ml), the solution was dried over anhydrous magnesium sulphate and the solvent removed at room temperature (0.05 mm) to give the crude product (3.65 g, 74%), which was suitable for photolysis (*vide infra*).

λ_{max} (Ether) 295 nm.

P.m.r. ($CDCl_3$, δ p.p.m.) 6.80 (q, 2H, $C_{3,6}$-olefinic protons adjacent to nitrogen); 5.77 (q, 2H, $C_{4,5}$-olefinic protons); 3.87 (s, 6H, *O*-methyl protons).

2,3-Dimethoxycarbonyl-2,3-diazabicyclo[2.2.0]hex-5-ene (82)

(a) By irradiation of 1,2-Dimethoxycarbonyl-1,2-diazacyclohexa-3,5-diene (86)

The crude diazacyclohexadiene (0.99 g, 5 mmole) in dry ether (125 ml, redistilled from sodium metal) was irradiated at 0° (AH lamp, pyrex filter). Care was taken to exclude oxygen from the reaction vessel by thorough initial purging with dry oxygen-free nitrogen and by slow passage of a nitrogen stream (pre-saturated with ether) during the irradiation. The course of the reaction was monitored by observing the disappearance of the diene absorption at 295 nm in the u.v. spectrum. (This was replaced by an absorption at 275 nm due to *N*, *N*'-dimethoxycarbonyl-2-aminopyrrole - a minor photoproduct). After 9 hours, the solution was evaporated at room temperature to *ca.* 20 ml, and some insoluble polymeric material filtered

off. Complete evaporation then gave a slightly yellow oil from which the diazabicyclohexene could be isolated by preparative scale t.l.c. (silica/5% ethyl acetate in chloroform) as a colourless oil (0.20 g, 20%).

The diazabicyclohexene showed end absorption only in the u.v. spectrum.

ν_{max} 778 m, 1111 ms, 1298 s(broad), 1445 s, 1730 s (broad), 2960 w cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 6.80 (m, 2H, $C_{5,6}$-olefinic protons); 5.26 (m, 2H, $C_{1,4}$-allylic cyclobutyl protons adjacent to nitrogen); 3.84 (s, 6H, *O*-methyl protons).

(b) By addition of Cyclobutadiene to Dimethyl Azodicarboxylate

A mixture of cyclobutadieneiron tricarbonyl (384 mg, 2 mmole) and dimethyl azodicarboxylate (292 mg, 2 mmole) in 95% ethanol (50 ml) was cooled to 0° in an ice bath and vigorously stirred while powdered ceric ammonium nitrate (8 g) was added. Carbon monoxide evolution ceased after a few minutes, and a slight excess of the inorganic salt remained undissolved.

The dark red reaction mixture was poured into cold water (100 ml) and extracted with chloroform (3 x 50 ml). The extracts were washed with water (3 x 50 ml) and dried over anhydrous magnesium sulphate before evaporation under reduced pressure. Preparative scale t.l.c. (silica/5% ethyl acetate in chloroform) allowed isolation of the diazabicyclohexene (130 mg, 31%), which was identical to that prepared by route (a). The yield was not improved by performing the oxidation under nitrogen, nor by more gradual addition of the ceric salt.

Attempted Addition of Dimethyl Azodicarboxylate to *exo*-1,6-Dimethyl-7,8-diphenyltricyclo[4.2.1.$0^{2,5}$]nona-3,7-dien-9-one (87)

The nonadienone (155 mg, 0.5 mmole) and the azodiester (73 mg, 0.5 mmole) in toluene (2 ml) were heated under reflux for 24 hours. The solvent was evaporated at room temperature (0.05 mm). A p.m.r. spectrum revealed that no reaction had occurred.

Attempted Photo-addition of Dimethyl Azodicarboxylate to *exo*-1,6-Dimethyl-7,8-diphenyltricyclo[4.2.1.$0^{2,5}$]nona-3,7-dien-9-ol (88)

The nonadienol* (312 mg, 1 mmole) and the azodiester (146 mg, 1 mmole) were dissolved in dry ether (5 ml) in a quartz tube and irradiated at 0° in a nitrogen atmosphere (AH lamp, pyrex filter). After 5 hours, the solution was evaporated to dryness at room temperature (12 mm). Inspection of the p.m.r. spectrum of the crude photolysate revealed that little, if any, of the alcohol had reacted, though hardly any of the azodiester remained.

Preparative scale t.l.c. (silica/chloroform) allowed recovery of the unreacted alcohol (255 mg, 82%). No other significant fraction was present.

8,9-Dimethoxycarbonyl-2,5-dimethyl-3,4-diphenyl-8,9-diazatetracyclo[4.4.0.$1^{2,5}$.$0^{7,10}$]undec-3-en-11-one (83)

2,3-Dimethoxycarbonyl-2,3-diazabicyclo[2.2.0]hex-5-ene (82) (198 mg, 1 mmole), 2,5-dimethyl-3,4-diphenyl-cyclopenta-2,4-dienone dimer (260 mg, 0.5 mmole) and benzene (10 ml) were heated under reflux for 4 hours.

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* Prepared by sodium borohydride reduction of the nonadienone (87) according to the published procedure[4].

A p.m.r. spectrum showed that complete reaction had occurred, and a slight excess of dienone dimer was present. Preparative scale t.l.c. (silica/5% ethyl acetate in chloroform) allowed separation of the required *product* (224 mg, 49%).

Two recrystallizations from ether/*n*-hexane gave colourless prisms, m.p. 177.5-178° (Found: C, 71.1; H, 5.6; N, 6.1. $C_{27}H_{26}N_2O_5$ requires C, 70.7; H, 5.7; N, 6.1%).

λ_{max} 248, 261 nm, ε 9200, 9900.

ν_{max} 769 ms, 1064 ms, 1128 ms, 1203 ms, 1300 s (broad), 1380 s, 1727 s, 1765 s cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.3-6.9 (m, 10H, aromatic protons); 4.46 (broad s, 2H, $C_{7,10}$-cyclobutyl protons adjacent to nitrogen); 3.87 (s, 6H, *O*-methyl protons); 3.15 (broad s, 2H, $C_{1,6}$-cyclobutyl protons); 1.30 (s, 6H, $C_{2,5}$-methyl protons).

m/e 458 (Molecular ion, 6%), 430 (1%), 258 (base peak), 198 (5%), 139 (11%), 59 (23%).

Photolysis of 8,9-Dimethoxycarbonyl-2,5-dimethyl-3,4-diphenyl-8,9-diazatetracyclo[4.4.0.$1^{2,5}$.$0^{7,10}$]undec-3-en-11-one (83) - Preparation of 1,2-Dimethoxycarbonyl-1,2-diazet-3-ine (84)

The ketone (137 mg, 0.3 mmole) was dissolved in deuteriochloroform (0.5 ml) in a thin quartz tube and irradiated at 0° (AH lamp, vycor filter) while the reaction was monitored by p.m.r. spectroscopy. After 4 hours, approximately one half of the ketone had reacted, and irradiation was stopped at this point.

Preparative scale t.l.c. (silica/chloroform) allowed isolation of the *diazetine* (17 mg, 63%, *ca.* 95% purity) as a

colourless oil, which could be stored for limited periods at 0°, but was generally used without delay.

ν_{max} (CCl_4) 1120 m, 1243 ms, 1301 ms, 1339 s, 1442 s, 1743 s, 1776 ms, 2962 mw, 3160 w cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 6.57 (s, 2H, $C_{3,4}$-olefinic protons); 3.88 (s, 6H, *O*-methyl protons).

m/e 172 (Molecular ion, 13%), 157 (9%), 142 (17%), 113 (24%), 59 (base peak). The mass spectrum also showed a significant M+2 peak at 174 (11%).

Unreacted starting material (65 mg) was readily recovered.

Catalytic Hydrogenation of 1,2-Dimethoxycarbonyl-1,2-diazet-3-ine (84)

10% Palladium on charcoal (2 mg) was suspended in methanol (5 ml) and saturated with hydrogen at atmospheric pressure. Freshly prepared diazetine (17 mg, 0.1 mmole) in methanol (5 ml) was then added, and the mixture vigorously stirred at room temperature while rapid uptake of 0.1 mmole of hydrogen occurred. The reaction mixture was filtered to remove the catalyst, poured into cold water (25 ml) and extracted with chloroform (3 x 15 ml). After washing with water (3 x 10 ml), the extracts were dried over anhydrous magnesium sulphate and evaporated to dryness. Preparative scale t.l.c. (silica/chloroform) followed by distillation (50°/0.05 mm) gave *1,2-dimethoxycarbonyl-1,2-diazetidine* (89) (9 mg, 53%) as a colourless oil.

The u.v. spectrum showed end absorption only.

ν_{max} (CCl_4) 1351 ms, 1444 ms, 1722 s, 1759 ms, 2962 w cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 4.34 (s, 4H, $C_{3,4}$-cyclobutyl protons); 3.87 (s, 6H, *O*-methyl protons).

m/e 174 (Molecular ion, 63%), 115 (35%), 102 (47%), 71 (base peak), 59 (89%).

Attempted Preparation of 1,2-Dimethoxycarbonyl-1,2-diazetidine (89) by Thermal Addition of Dimethyl Azodicarboxylate to Ethylene

A stainless steel tube of 200 ml capacity was flushed out with nitrogen and charged with dimethyl azodicarboxylate (7.3 g, 0.05 mole) and ethylene gas to a pressure of 100 psi. The tube was then sealed and heated in a furnace at 180° for 6 hours. After cooling, the tube was washed out with acetone, which was then evaporated under reduced pressure leaving a dark brown oil. Preliminary purification of this crude material was achieved by distillation (60°/0.05 mm) which gave a colourless oil (1.9 g). Inspection of the p.m.r. spectrum showed that this was a complex mixture of products, partial separation of which was possible by preparative scale t.l.c. (silica/chloroform). However, no fraction showed the expected p.m.r. or mass spectrum (*m/e* 174 was negligible for all fractions and for the crude reaction mixture).

Attempted Reaction of 1,2-Dimethoxycarbonyl-1,2-diazet-3-ine (84) with:

(a) Cyclopentadiene

To the diazetine (17 mg, 0.1 mmole) in deuteriochloroform (0.4 ml) was added freshly redistilled cyclopentadiene (13 mg, 0.2 mmole). After 6 hours at room temperature, a p.m.r. spectrum suggested that although most of the diazetine had disappeared, reaction with the diene had not occurred. This was confirmed by preparative scale t.l.c. (silica/chloroform), when no product was found and only a trace of the diazetine was recovered.

(b) 3,6-Di(2'-pyridyl)-*s*-tetrazine

To the diazetine (17 mg, 0.1 mmole) in deuteriochloroform (0.4 ml) was added the *s*-tetrazine (24 mg, 0.1 mmole). No gas evolution or decolourization occurred, and after 2 hours, a p.m.r. spectrum showed that no reaction had taken place.

Thermal Isomerization of 1,2-Dimethoxycarbonyl-1,2-diazet-3-ine (84) to 1,4-Dimethoxycarbonyl-1,4-diazabuta-1,3-diene (92)

The diazetine (17 mg, 0.1 mmole) in deuteriochloroform (0.4 ml) was stored at room temperature. Periodic p.m.r. spectra showed that conversion to the diazabutadiene amounted to 18% after 2 hours, 39% after 5 hours, and 65% after 10 hours. These figures correspond to a first-order half-life of 6.9 hours at this temperature.

At 34°, isomerization was much more rapid. After ½ hour, 17% isomerization had taken place; after 1 hour, 32%; after 1½ hours, 44%; after 2 hours, 54%; and after 2½ hours, 63%. The half-life at this temperature was calculated as 1.8 hours.

The product, *1,4-dimethoxycarbonyl-1,4-diazabuta-1,3-diene* slowly polymerized in solution even at 0°, and quite rapidly on attempted isolation.

P.m.r. ($CDCl_3$, δ p.p.m.) 8.36 (s, 2H, $C_{2,3}$-olefinic protons); 3.98 (s, 6H, *O*-methyl protons).

Attempted Addition of Ethyl Vinyl Ether to 1,4-Dimethoxycarbonyl-1,4-diazabuta-1,3-diene (92)

To a mixture of the diazetine and the diazabutadiene (*ca.* 1:1, 17 mg, 0.1 mmole) in deuteriochloroform (0.4 ml) was added an excess of ethyl vinyl ether (22 mg, 0.3 mmole). After about 6 hours, a p.m.r. spectrum showed that neither

diaza compound remained, though no product appeared to have been formed. This was confirmed by t.l.c. (silica/chloroform).

anti, cis-3,4-Dichloro-1-methyl-7,8; 9,10-dibenzotricyclo-[4.2.2.$0^{2,5}$]deca-7,9-diene (100b)

9-Methylanthracene (0.96 g, 5 mmole) and *cis*-3,4-dichlorocyclobutene (1.54 g, 12.5 mmole) were heated together in an oil bath at 150° for 10 hours. The excess cyclobutene was recovered by evaporation in vacuum and the residue triturated with ether/*n*-hexane to give the crystalline *product* (1.30 g, 83%), which was filtered off and washed with *n*-hexane.

Recrystallization from *n*-hexane yielded large colourless crystals, m.p. 119.5-120° (Found: C, 72.6; H, 5.25; Cl, 22.6. $C_{19}H_{16}Cl_2$ requires C, 72.4; H, 5.1; Cl, 22.5%).

λ_{max} 266.5, 273.5 nm, ε 1050, 1250.

ν_{max} 680 m, 754 s, 767 s, 803 m, 955 m, 1261 m, 1381 m cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.5-7.1 (m, 8H, aromatic protons); 4.51 (d (J=3.5 Hz), 1H, C_6-bridgehead proton); 3.8-3.4 (m, 2H, $C_{3,4}$-cyclobutyl protons); 3.2-2.6 (m, 2H, $C_{2,5}$-cyclobutyl protons); 1.93 (s, 3H, C_1-methyl protons).

m/e * 314 (Molecular ion, 18%), 279 (11%), 243 (10%), 228 (11%), 192 (base peak), 191 (22%).

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* In this, and all following halogen-containing compounds, only the parent ions are quoted. In all cases, the correct isotopic abundances were observed.

anti, cis-3,4-Dichloro-1,6-dimethyl-7,8; 9,10-dibenzotricyclo-[4.2.2.$0^{2,5}$]deca-7,9-diene (100c)

9,10-Dimethylanthracene (2.06 g, 0.01 mole) and *cis*-3,4-dichlorocyclobutene (3.07 g, 0.025 mole) were heated together in an oil bath at 150° for 5 hours. After cooling, ether (5 ml) was added, and the product (2.94 g, 92%) was filtered off, and washed with methanol. The colourless prisms had m.p. 145-146° (lit.[97] 147°).

ν_{max} 746 ms, 754 s, 1384 s, 1457 s, 2971 s, 3042 m cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.5-7.1 (m (AA'BB'), 8H, aromatic protons); 3.53 (m, 2H, $C_{3,4}$-cyclobutyl protons); 2.70 (m, 2H, $C_{2,5}$-cyclobutyl protons); 1.93 (s, 6H, $C_{1,6}$-methyl protons).

1-Bromo-*anti, cis*-3,4-dichloro-7,8; 9,10-dibenzotricyclo-[4.2.2.$0^{2,5}$]deca-7,9-diene (100d)

9-Bromoanthracene (2.57 g, 0.01 mole) and *cis*-3,4-dichlorocyclobutene (3.07 g, 0.025 mole), were heated together in an oil bath at 150° for 10 hours. The excess cyclobutene was removed in vacuum, and the residual dark coloured oil was put onto a 2½ x 30 cm alumina column. Elution with cyclohexane gave a yellow oil, which crystallized on storing overnight.

Recrystallization from *n*-hexane gave the *product* (2.46 g, 65%). An analytical sample, m.p. 144-145°, was obtained by an additional recrystallization from *n*-hexane (Found: C, 56.7; H, 3.25; Cl, 18.8; Br, 20.7. $C_{18}H_{13}Cl_2Br$ requires C, 56.9; H, 3.45; Cl, 18.7; Br, 21.0%).

λ_{max} 265.5, 272.5 nm, ε 670, 710.

ν_{max} 680 m, 752 s, 760 s, 939 s cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 8.0-7.1 (m, 8H, aromatic

protons); 4.49 (d (J=3.4 Hz), 1H, C_6-bridgehead proton); 3.64 (m, 2H, $C_{3,4}$-cyclobutyl protons); 3.3-2.9 (m, 2H, $C_{2,5}$-cyclobutyl protons).

*m/e** 378 (Molecular ion, 18%), 299 (14%), 263 (18%), 256 (base peak), 228 (65%), 202 (26%), 178 (30%), 176 (24%).

7,8; 9,10-Dibenzotricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (101a)

Granulated sodium metal (0.56 g, 25 mmole) was added to a solution of resublimed naphthalene (3.2 g, 25 mmole) in glyme (30 ml, redistilled from sodium aluminium hydride) and the mixture stirred at room temperature under dry oxygen-free nitrogen for 30 minutes, when the sodium had dissolved.

The resulting dark green solution was cooled to *ca.* -60° in an acetone/dry ice bath, then slowly added, under nitrogen, to a cooled (*ca.* -60°) solution of 1-bromo-*anti*, *cis*-3,4-dichloro-7,8; 9,10-dibenzotricyclo[4.2.2.$0^{2,5}$]deca-7,9-diene (100d) (1.52 g, 4 mmole) in dry glyme (10 ml) until a dark green colour persisted. (The precise end-point was difficult to determine). The reaction mixture was then poured immediately into cold water (100 ml), and extracted with chloroform (3 x 50 ml). After washing with water (2 x 50 ml), the extracts were dried over anhydrous magnesium sulphate and evaporated to dryness.

The naphthalene was removed by sublimation at 40° (0.05 mm) and the light yellow crystalline residue was extracted with ethanol (100 ml), treated with decolourizing charcoal, and evaporated to *ca.* 10 ml, when the product (0.49 g, 53%) crystallized as fine colourless needles, m.p. 138-139° (lit.[97] 137°).

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* See footnote page 100.

λ_{max} 267, 274 nm, ε 1200, 1300.

ν_{max} 744 s, 763 m, 832 m, 973 m, 1299 m, 1380 m cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.17 (m, 8H, aromatic protons); 5.91 (s, 2H, $C_{3,4}$-olefinic protons); 4.27 (m, 2H, $C_{1,6}$-bridgehead protons); 2.96 (m, 2H, $C_{2,5}$-cyclobutyl protons).

m/e 230 (Molecular ion, 60%), 178 (base peak).

1-Methyl-7,8; 9,10-dibenzotricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (101b)

Granulated sodium (0.56 g, 25 mmole) was added to a solution of resublimed naphthalene (3.2 g, 25 mmole) in glyme (30 ml, redistilled from sodium aluminium hydride) under dry oxygen-free nitrogen and the mixture stirred at room temperature for 30 minutes, when the sodium had dissolved.

The resulting dark green solution was then cooled to *ca.* -60° by means of an acetone/dry ice bath, and slowly added to solution of the *anti, cis*-dichloride (100b) (0.95 g, 3 mmole) in dry glyme (10 ml) at -60° under nitrogen. A slight excess was present when the colour changed from light yellow to dark green, the reaction mixture being immediately quenched in cold water (100 ml) and extracted with chloroform (3 x 50 ml). The extracts were washed with water (2 x 50 ml), dried over anhydrous magnesium sulphate and evaporated to dryness. Sublimation (40°, 0.05 mm) removed the naphthalene, and left the crystalline *product* (0.72 g, 98%).

Recrystallization from ethanol yielded fine colourless needles, m.p. 97-98° (Found: C, 93.5; H, 6.6. $C_{19}H_{16}$ requires C, 93.4; H, 6.6%).

λ_{max} 267, 274 nm, ε 1300, 1600.

ν_{max} 675 m, 744 s, 758 m, 844 m, 968 s, 1295 m,

1378 s cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.23 (m, 8H, aromatic protons); 5.96 (s, 2H, $C_{3,4}$-olefinic protons); 4.27 (d (J=3.8 Hz), 1H, C_6-bridgehead proton); 3.04 (t, 1H, C_5-cyclobutyl proton); 2.58 (d (J=4.4 Hz), 1H, C_2-cyclobutyl proton); 1.90 (s, 3H, C_1-methyl protons).

m/e 244 (Molecular ion, 48%), 229 (27%), 192 (base peak).

1,6-Dimethyl-7,8; 9,10-dibenzotricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (101c)

Granulated sodium (1.13 g, 0.05 mole) was added to a solution of resublimed naphthalene (6.4 g, 0.05 mole) in glyme (50 ml, redistilled from sodium aluminium hydride), and the mixture stirred magnetically at room temperature under dry oxygen-free nitrogen for 30 minutes, when the sodium had dissolved.

The resulting dark green solution was cooled to *ca.* -60° in an acetone/dry ice bath, then slowly added to a solution of the *anti, cis*-dichloride (101c) (2.63 g, 8 mmole) in dry glyme (20 ml) at -60°, under nitrogen, while the colour changed from yellow to red to green. The reaction mixture was immediately poured into cold water (200 ml), extracted with chloroform (3 x 100 ml), washed with water (2 x 100 ml), dried over anhydrous magnesium sulphate and evaporated to dryness in vacuum.

Sublimation at 40° (0.05 mm) removed the naphthalene, and the crystalline residue (1.90 g, 92%), m.p. 90-94° (lit.[97] 96°) was the required product. This was suitable for the preparation of adducts.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.18 (m, 8H, aromatic protons); 5.92 (s, 2H, $C_{3,4}$-olefinic protons); 2.67 (s, 2H,

$C_{2,5}$-cyclobutyl protons); 1.85 (s, 6H, $C_{1,6}$-methyl protons).

4,7-Dimethyl-5,6-diphenyl-11,12; 13,14-dibenzopentacyclo-[8.2.2.$1^{4,7}$.$0^{2,9}$.$0^{3,8}$]pentadeca-5,11,13-trien-15-one (102a)

Cyclobutene (101a) (0.40 g, 1.75 mmole), 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone dimer (0.45 g, 0.875 mmole) and benzene (20 ml) were heated under reflux for 20 hours. Evaporation to dryness under reduced pressure and trituration with ether (10 ml) gave the crystalline *product* (0.56 g, 64%).

An analytical sample was obtained by recrystallization from ether, as colourless prisms, m.p. 239-240°, with decomposition (Found: C, 90.7; H, 6.4. $C_{37}H_{30}O$ requires C, 90.6; H, 6.2%).

λ_{max} 250, 267, 273 nm, ε 9200, 10700, 10300.

ν_{max} 703 s, 714 s, 756 ms, 768 s, 1381 ms, 1770 s cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.5-6.8 (m, 18H, aromatic protons); 4.35 (m, 2H, $C_{1,10}$-bridgehead protons); 2.20 (m, 2H, $C_{2,9}$-cyclobutyl protons); 1.67 (m, 2H, $C_{3,8}$-cyclobutyl protons); 1.20 (s, 6H, $C_{4,7}$-methyl protons).

m/e 490 (Molecular ion, 0.8%), 462 (18%), 258 (81%), 204 (base peak), 203 (36%), 202 (17%), 191 (15%), 178 (25%).

1,4,7-Trimethyl-5,6-diphenyl-11,12; 13,14-dibenzopentacyclo-[8.2.2.$1^{4,7}$.$0^{2,9}$.$0^{3,8}$]pentadeca-5,11,13-trien-15-one (102b)

Cyclobutene (101b) (0.49 g, 2 mmole) and 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone dimer (0.52 g, 1 mmole) were refluxed together in benzene (20 ml) for 24 hours. After removal of the solvent under reduced pressure, trituration with ether (20 ml) gave the *adduct* (0.77 g, 72%) as a crystalline solid.

Recrystallization from ether yielded colourless prisms, m.p. 226-227°, with decomposition (Found: C, 90.3;

H, 6.2. $C_{38}H_{32}O$ requires C, 90.4; H, 6.4%).

λ_{max} 250, 267, 273 nm, ε 9700, 11100, 10600.

ν_{max} 701 s, 713 s, 757 s, 769 s, 1381 s, 1770 s cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.5-6.8 (m, 18H, aromatic protons); 4.33 (d (J=4.1 Hz), 1H, C_{10}-bridgehead proton); 2.4-1.3 (m, 4H, $C_{2,3,8,9}$-cyclobutyl protons); 1.86 (s, 3H, C_1-methyl protons); 1.20 and 1.16 (s, s, 3H, 3H, C_4- and C_7-methyl protons).

m/e 504 (Molecular ion, 0.12%), 476 (5%), 258 (56%), 218 (base peak), 203 (37%), 202 (10%), 192 (15%).

1,4,7,10-Tetramethyl-5,6-diphenyl-11,12; 13,14-dibenzo-pentacyclo[8.2.2.$1^{4,7}$.$0^{2,9}$.$0^{3,8}$]pentadeca-5,11,13-trien-15-one (102c)

Cyclobutene (101c) (1.81 g, 7 mmole), 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone dimer (1.82 g, 3.5 mmole), and benzene (20 ml) were heated under reflux for 20 hours. The solvent was evaporated under reduced pressure, and the residue triturated with ether (20 ml) to give the crude *product* (3.02 g, 83%).

Recrystallization from chloroform/*n*-hexane yielded colourless crystals, m.p. 220-221°, with decomposition (Found: C, 90.2; H, 6.5. $C_{39}H_{34}O$ requires C, 90.3; H, 6.6%).

λ_{max} 250, 266, 273 nm, ε 9600, 10500, 9900.

ν_{max} 753 ms, 760 m, 1380 s, 1770 s cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.4-6.8 (m, 18H, aromatic protons); 1.91 (m, 2H, $C_{2,9}$-cyclobutyl protons); 1.86 (s, 6H, $C_{1,10}$-methyl protons); 1.53 (m, 2H, $C_{3,8}$-cyclobutyl protons); 1.16 (s, 6H, $C_{4,7}$-methyl protons).

m/e 518 (Molecular ion, 0.08%), 490 (11%), 258 (31%), 232 (base peak), 217 (49%), 202 (10%).

Photolysis of 1,4,7,10-Tetramethyl-5,6-diphenyl-11,12; 13,14-dibenzopentacyclo[8.2.2.$1^{4,7}$.$0^{2,9}$.$0^{3,8}$]pentadeca-5,11,13-trien-15-one (102c)

The ketone (26 mg, 0.05 mmole) was dissolved in deuteriochloroform (0.1 ml) in a thin quartz tube and irradiated at 0° (AH lamp, vycor filter). P.m.r. spectra recorded at half-hourly intervals showed that after 2 hours, only 5% of the starting material remained and three major products had been formed.

1,4-Dimethyl-2,3-diphenylbenzene (77) and 1,4-dimethyl-2,3; 5,6-dibenzobicyclo[2.2.2]octa-2,5,7-triene (99c) were each present in about 30% yield. The third product was not identified.

4,7-Dimethyl-5,6-diphenyl-11,12; 13,14-dibenzotetracyclo-[8.2.2.$0^{2,9}$.$0^{3,8}$]tetradeca-4,6,11,13-tetraene (103a)

Ketone (102a) (0.34 g, 0.7 mmole) was heated just above the melting point in a Wood's Metal bath (245°) for 15 minutes, when carbon monoxide evolution had ceased. The residue was taken up in *n*-hexane (25 ml), treated with decolourizing charcoal, and evaporated to 5 ml when the *product* (0.20 g, 62%) crystallized from solution.

Recrystallization from *n*-hexane gave slightly yellow needles, m.p. 192-194° (Found: C, 93.2; H, 6.8. $C_{36}H_{30}$ requires C, 93.5; H, 6.5%).

λ_{max} 248, 266 (infl.), 274, 305 (infl.) nm, ε 11500, 7800, 6700, 3200.

ν_{max} 704 s, 761 ms, 772 ms, 1380 ms, 1493 m, 1604 m cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.5-6.6 (m, 18H, aromatic protons); 4.43 (m, 2H, $C_{1,10}$-bridgehead protons); 2.72 (m, 2H, $C_{2,9}$-cyclobutyl protons); 2.14 (m, 2H, $C_{3,8}$-cyclobutyl

protons); 1.47 (s, 6H, $C_{4,7}$-methyl protons).

m/e 462 (Molecular ion, 4%), 258 (76%), 204 (base peak), 203 (35%), 202 (15%), 191 (13%), 178 (11%).

1,4,7-Trimethyl-5,6-diphenyl-11,12; 13,14-dibenzotetracyclo-[8.2.2.$0^{2,9}$.$0^{3,8}$]tetradeca-4,6,11,13-tetraene (103b)

Ketone (102b) (0.38 g, 0.75 mmole) was heated just above the melting point in a Wood's Metal bath (235°) for 20 minutes, when carbon monoxide evolution had ceased. The residue was taken up in *n*-hexane (25 ml), treated with decolourizing charcoal, and evaporated to 5 ml. On cooling, the *product* (0.29 g, 82%) crystallized as light yellow prisms.

Two recrystallizations from *n*-hexane yielded colourless prisms, m.p. 218-220° (Found: C, 93.3; H, 6.9. $C_{37}H_{32}$ requires C, 93.2; H, 6.8%).

λ_{max} 248, 267 (infl.), 274, 306 (infl.) nm, ε 11700, 8100, 6900, 3300.

ν_{max} 705 s, 764 s, 772 s, 1379 s, 1492 m, 1603 m cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.5-6.6 (m, 18H, aromatic protons); 4.42 (d (J=4.0 Hz), 1H, C_{10}-bridgehead proton); 3.0-1.8 (m, 4H, $C_{2,3,8,9}$-cyclobutyl protons); 1.95 (s, 3H, C_1-methyl protons); 1.48 (s, 6H, $C_{4,7}$-methyl protons).

m/e 476 (Molecular ion, 6%), 258 (62%), 218 (base peak), 203 (50%), 202 (18%), 192 (7%).

1,4,7,10-Tetramethyl-5,6-diphenyl-11,12; 13,14-dibenzotetracyclo[8.2.2.$0^{2,9}$.$0^{3,8}$]tetradeca-4,6,11,13-tetraene (103c)

Ketone (102c) (2.59 g, 5 mmole) was heated just above the melting point in a Wood's Metal bath (240°) for 10 minutes, when carbon monoxide evolution was complete. After cooling, the residue was dissolved in warm *n*-hexane (25 ml), treated with decolourizing charcoal, filtered,

evaporated to 5 ml and cooled to give the *product* (1.89 g, 77%).

Recrystallization from *n*-hexane yielded colourless needles, m.p. 220-222° (Found: C, 93.3; H, 6.9. $C_{38}H_{34}$ requires C, 93.0; H, 7.0%).

λ_{max} 247, 265 (infl.), 273, 305 (infl.) nm, ε 12200, 8400, 7200, 3700.

ν_{max} 703 m, 757 s, 1380 s, 1452 s, 1492 w, 1608 w cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.5-6.5 (m, 18H, aromatic protons); 2.44 (m, 2H, $C_{2,9}$-cyclobutyl protons); 2.00 (m, 2H, $C_{3,8}$-cyclobutyl protons); 1.98 (s, 6H, $C_{1,10}$-methyl protons); 1.43 (s, 6H, $C_{4,7}$-methyl protons).

m/e 490 (Molecular ion, 8%), 258 (36%), 232 (base peak), 217 (59%), 202 (14%).

2,3; 5,6-Dibenzobicyclo[2.2.2]octa-2,5,7-triene (99a)

4,7-Dimethyl-5,6-diphenyl-11,12; 13,14-dibenzotetracyclo[8.2.2.$0^{2,9}$.$0^{3,8}$]tetradeca-4,6,11,13-tetraene (103a) (138 mg, 0.3 mmole) was dissolved in deuteriochloroform (0.5 ml) in a thin quartz tube under oxygen-free nitrogen and irradiated at 0° (AH lamp, vycor filter). After 6 hours, 75% of the starting material had been converted to photoproducts, which were separated by preparative scale t.l.c. (silica/carbon tetrachloride).

The crude dibenzobarrelene [23 mg, 48% calculated from unrecovered (103a)] was obtained as a colourless oil which slowly crystallized, and was further purified by g.l.c. (6' x 3/8" column of 10% SE30 on Embacel, 185°, retention time 3.7 mins). The white crystalline solid had m.p. 120.5-121° (lit.[92] 119.5-120.5°). 30 mg of the starting material was recovered.

λ_{max} 252, 258.5 (infl.), 266 (infl.), 272.5, 279.5 nm,

ε 1600, 870, 1050, 2200, 3400.

ν_{max} (CCl_4) 685 s, 1150 w, 1320 w, 1459 m, 1470 w, 2959 w, 3006 w, 3058 w cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.45-6.9 (m, 10H, aromatic and $C_{7,8}$-olefinic protons); 5.19 (dd, 2H, $C_{1,4}$-bridgehead protons).

m/e 204.0934 (Molecular ion and base peak, $C_{16}H_{12}$ requires 204.0939), 203 (85%), 202 (62%), 178 (16%).

1-Methyl-2,3; 5,6-dibenzotricyclo[2.2.2]octa-2,5,7-triene (99b)

1,4,7-Trimethyl-5,6-diphenyl-11,12; 13,14-dibenzo-tetracyclo[8.2.2.$0^{2,9}$.$0^{3,8}$]tetradeca-4,6,11,13-tetraene (103b) (119 mg, 0.25 mmole) was dissolved in deuterio-chloroform (0.5 ml) in a thin quartz tube under oxygen-free nitrogen, and irradiated at 0° (AH lamp, vycor filter). After 90 minutes, a p.m.r. spectrum showed that only 10% of the starting material remained.

Preparative scale t.l.c. (silica/carbon tetrachloride) permitted separation of the required *product* (38 mg, 69%) in about 95% purity. A pure sample was obtained as a white crystalline solid, m.p. 96-97°, by g.l.c. (6' x 3/8" column of 10% SE30 on Embacel, 200°, retention time 6.6 mins) (Found: C, 93.3; H, 6.7. $C_{17}H_{14}$ requires C, 93.5; H, 6.5%).

λ_{max} 254, 259 (infl.), 266 (infl.), 272.5, 280 nm, ε 1200, 870, 950, 2200, 3400.

ν_{max} (CCl_4) 682 s, 1326 m, 1379 m, 1449 ms, 1460 ms, 2960 ms, 3002 m, 3052 ms cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.45-6.9 (m, 9H, aromatic and C_8-olefinic protons); 6.64 (m, 1H, C_7-olefinic proton); 5.10 (m, 1H, C_4-bridgehead proton); 2.16 (s, 3H, C_1-methyl protons).

m/e 218.1090 (Molecular ion, 80%, $C_{17}H_{14}$ requires

218.1095), 203 (base peak), 202 (41%).

1,4-Dimethyl-2,3; 5,6-dibenzobicyclo[2.2.2]octa-2,5,7-triene (99c)

1,4,7,10-Tetramethyl-5,6-diphenyl-11,12; 13,14-dibenzotetracyclo[8.2.2.$0^{2,9}$.$0^{3,8}$]tetradeca-4,6,11,13-tetraene (103c) (98 mg, 0.2 mmole) was dissolved in deuteriochloroform (0.5 ml) in a thin quartz tube under dry oxygen-free nitrogen, and irradiated at 0° (AH lamp, vycor filter). Periodic p.m.r. spectra showed that 80% conversion to photoproducts had occurred after 4 hours.

The *dibenzobarrelene* (33 mg, 72%) was isolated in *ca.* 95% purity by preparative scale t.l.c. (silica/carbon tetrachloride). A pure sample was obtained by g.l.c. (6' x 3/8" column of 10% SE30 on Embacel, 210°, retention time 8.4 mins), as a white crystalline solid, m.p. 112-114° (Found: C, 93.1; H, 7.2. $C_{18}H_{16}$ requires C, 93.1; H, 6.9%).

λ_{max} 254, 259 (infl.), 266, 273, 280.5 nm, ε 1700, 1250, 1300, 2300, 3400.

ν_{max} (CCl_4) 689 s, 1030 m, 1336 m, 1385 ms, 1448 s, 1459 s, 2866 w, 2930 w, 2960 m, 3004 w, 3056 w cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.4-6.9 (m, 8H, aromatic protons); 6.64 (s, 2H, $C_{7,8}$-olefinic protons); 2.15 (s, 6H, $C_{1,4}$-methyl protons).

m/e 232.1241 (Molecular ion, 63%, $C_{18}H_{16}$ requires 232.1252), 217 (base peak), 202 (33%).

4,7-Dimethyl-5,6-diphenyl-11,12-benzopentacyclo-[8.2.2.$1^{4,7}$.$0^{2,9}$.$0^{3,8}$]pentadeca-5,11,13-trien-15-one (106)

7,8-Benzotricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (105) (prepared by dechlorination, with disodium dihydrophenanthrenedi-ide, of the adduct (104) of benzyne and

7,8-dichlorobicyclo[4.2.0]octa-2,4-diene)* (0.27 g, 1.5 mmole), 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone dimer (0.39 g, 0.75 mmole) and benzene (25 ml) were heated under reflux for 24 hours. Preparative scale t.l.c. (silica/benzene) allowed separation of the *adduct* (0.58 g, 88%). Recrystallization from ether yielded fine white needles, m.p. 233.5-234°, with decomposition (Found: C, 90.3; H, 6.5. $C_{33}H_{28}O$ requires C, 90.0; H, 6.4%).

λ_{max} 250, 263, 271 nm, ε 9200, 10000, 9200.

ν_{max} 700 s, 757 s, 1441 ms, 1470 s, 1767 s cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.3-6.9 (m, 14H, aromatic protons); 6.71 (dd, 2H, $C_{13,14}$-olefinic protons); 4.03 (broad m, 2H, $C_{1,10}$-bridgehead protons); 2.10 (m, 2H, $C_{3,8}$-cyclobutyl protons); 1.95 (m, 2H, $C_{2,9}$-cyclobutyl protons); 1.23 (s, 6H, $C_{4,7}$-methyl protons).

m/e 440 (Molecular ion, 3%), 412 (29%), 258 (base peak), 154 (66%).

4,7-Dimethyl-5,6-diphenyl-11,12-benzotetracyclo-[8.2.2.$0^{2,9}$.$0^{3,8}$]tetradeca-4,6,11,13-tetraene (107)

4,7-Dimethyl-5,6-diphenyl-11,12-benzopentacyclo-[8.2.2.$1^{4,7}$.$0^{2,9}$.$0^{3,8}$]pentadeca-5,11,13-trien-15-one (106) (440 mg, 1 mmole) was placed in an n.m.r. tube and heated just above the melting point in a Wood's Metal bath (245°) for 10 minutes, when carbon monoxide evolution had ceased. Preparative scale t.l.c. (silica/carbon tetrachloride) gave the *tetraene* (338 mg, 82%). Recrystallization from *n*-hexane yielded almost colourless prisms, m.p. 145-147° (Found: C, 92.9; H, 6.9. $C_{32}H_{28}$ requires C, 93.2; H, 6.8%).

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* Kindly provided by Mr. G.M. Priestley.

λ_{max} 249, 300 (infl.) nm, ε 11000, 3600.

ν_{max} 703 s, 712 s, 753 s, 1380 m, 1470 s, 1607 w cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.25-6.9 (m, 14H, aromatic protons); 6.77 (dd, 2H, $C_{13,14}$-olefinic protons); 4.12 (broad m, 2H, $C_{1,10}$-bridgehead protons); 2.40 (m, 4H, $C_{2,3,8,9}$-cyclobutyl protons); 1.53 (s, 6H, $C_{4,7}$-methyl protons).

m/e 412 (Molecular ion, 15%), 258 (base peak), 154 (32%).

2,3-Benzobicyclo[2.2.2]octa-2,5,7-triene (98)

4,7-Dimethyl-5,6-diphenyl-11,12-benzotetracyclo-[8.2.2.$0^{2,9}$.$0^{3,8}$]tetradeca-4,6,11,13-tetraene (107) (86 mg, 0.21 mmole) and deuteriochloroform (0.5 ml) were placed in a thin quartz tube and irradiated at 0° (AH lamp, vycor filter). After 3 hours, 75% reaction had occurred (p.m.r.) and the products were separated by preparative scale t.l.c. (silica/carbon tetrachloride).

2,3-Benzobicyclo[2.2.2]octa-2,5,7-triene was purified by sublimation, which yielded colourless crystals (5 mg, 20%*) m.p. 63-64° (lit.[92] 65.0-65.5°).

λ_{max} 255 (infl.), 263, 269.5, 277 nm, ε 640, 660, 840, 860.

ν_{max} (CCl_4) 665 s, 700 s, 1199 m, 1227 m, 1332 s, 1459 ms, 1468 s, 2977 w, 3007 w, 3085 mw cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.4-6.8 (dd superimposed on a multiplet, 8H, aromatic and $C_{5,6,7,8}$-olefinic protons);

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* This rather poor isolated yield was due in part to the difficulty of isolating the product on this very small scale.

4.97 (broad m, 2H, $C_{1,4}$-bridgehead protons).

m/e 154 (Molecular ion, 83%), 153 (base peak), 152 (35%), 128 (26%), 76 (14%).

7,8-Bis(trifluoromethyl)tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (108), and 5,6,11,12-Tetrakis(trifluoromethyl)pentacyclo-[8.2.2.$2^{4,7}$.$0^{2,9}$.$0^{3,8}$]hexadeca-5,11,13,15-tetraene (113)

Cyclooctatetraene (10.4 g, 0.1 mole), hexafluorobut-2-yne (16.2 g, 0.1 mole) and hydroquinone (0.1 g) were sealed into an evacuated (*ca.* 10^{-3} mm) thick-walled pyrex tube (450 ml capacity) and heated at 120-128° for 16 hours. The tube was opened to a vacuum system, allowing recovery of unreacted hexafluorobut-2-yne (4.2 g).

Crystalline *5,6,11,12-tetrakis(trifluoromethyl)pentacyclo*[*8.2.2.*$2^{4,7}$*.*$0^{2,9}$*.*$0^{3,8}$]*hexadeca-5,11,13,15-tetraene* (1.4 g) was filtered from the reaction mixture, and washed well with benzene. Recrystallization from carbon tetrachloride yielded fine colourless needles, m.p. (sealed tube) 209-210° (Found: C, 50.0; H, 2.4; F, 47.6. $C_{20}H_{12}F_{12}$ requires C, 50.0; H, 2.5; F, 47.5%).

λ_{max} (Ether) 294 nm, ε 100.

ν_{max} 719 s, 900 m, 1080 ms, 1121 s, 1140 s, 1188 s, 1251 ms, 1279 s, 1293 s, 1302 s, 1673 m, 2908 w cm^{-1}.

P.m.r. (Acetone-d_6, δ p.p.m.) 6.73 (dd, 4H, $C_{13,14,15,16}$-olefinic protons); 4.31 (broad m, 4H, $C_{1,4,7,10}$-bridgehead protons); 1.82 (m, 4H, $C_{2,3,8,9}$-cyclobutyl protons).

^{19}F n.m.r. (Acetone, δ p.p.m.) 16.4 (s).

m/e (15 eV) 480 (Molecular ion, 1%), 266 (10%), 214 (27%), 197 (7%), 52 (base peak).

The remaining light yellow liquid was then distilled. A forerun (4.6 g) consisted of unreacted cyclooctatetraene,

o-bis(trifluoromethyl)benzene (50), and 7,8-bis(trifluoromethyl)tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (108) (5:6:4), while pure (108) (10.2 g, 38%) was collected at 60-61°/5 mm (lit.[85] 56-56.5°/4.8 mm).

ν_{max} (liquid film) 713 s, 755 s, 784 s, 1010 s, 1029 s, 1120-1190 s, 1249 s, 1292 s, 1319 s, 1362 ms, 1673 ms, 2902 m, 2974 w, 3024 w, 3090 w cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 6.17 (dd, 2H, $C_{9,10}$-olefinic protons); 6.09 (s, 2H, $C_{3,4}$-olefinic protons); 3.92 (broad m, 2H, $C_{1,6}$-bridgehead protons); 2.73 (m, 2H, $C_{2,5}$-cyclobutyl protons).

^{19}F n.m.r. (Acetone, δ p.p.m.) 16.6 (s).

m/e 266 (Molecular ion, 1%), 214 (10%), 197 (7%), 195 (16%), 177 (16%), 145 (16%), 52 (base peak).

Pyrolysis of 5,6,11,12-Tetrakis(trifluoromethyl)pentacyclo-[8.2.2.$2^{4,7}$.$0^{2,9}$.$0^{3,8}$]hexadeca-5,11,13,15-tetraene (113)

The pentacyclohexadecatetraene (48 mg, 0.1 mmole) was sealed into an n.m.r. tube and heated in a Wood's Metal bath at 220° for 5 minutes. A p.m.r. spectrum showed that quantitative cycloreversion to *o*-bis(trifluoromethyl)benzene (50) and 7,8-bis(trifluoromethyl)tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (108) had occurred, with little further decomposition. The retention times of the products on a 6' x 3/8" column of SE30 (10%) on Embacel at 70° were identical with those of authentic samples [(50), 2.5 mins and (108), 9.6 mins].

11,12-Bis(trifluoromethyl)-4,7-dimethyl-5,6-diphenylpentacyclo[8.2.2.$1^{4,7}$.$0^{2,9}$.$0^{3,8}$]pentadeca-5,11,13-trien-15-one (109)

7,8-Bis(trifluoromethyl)tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (108) (2.66 g, 10 mmole), 2,5-dimethyl-3,4-

diphenylcyclopenta-2,4-dienone dimer (2.60 g, 5 mmole) and benzene (10 ml) were heated under reflux for 20 hours. The benzene was evaporated and the residue triturated with ether/*n*-hexane to give the crystalline *product* (4.42 g, 84%). Recrystallization from ether/*n*-hexane yielded colourless crystals, m.p. 175-176° (Found: C, 70.5; H, 4.7; F, 21.0. $C_{31}H_{24}F_6O$ requires C, 70.7; H, 4.6; F, 21.65%).

λ_{max} 261 nm, ε 8900.

ν_{max} 700 ms, 721 ms, 1130 ms, 1146 ms, 1189 ms, 1288 ms, 1669 m, 1770 s cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.3-6.8 (m, 10H, aromatic protons); 6.55 (dd, 2H, $C_{13,14}$-olefinic protons); 4.14 (broad m, 2H, $C_{1,10}$-bridgehead protons); 2.07 (m, 2H, $C_{2,9}$-cyclobutyl protons); 1.93 (m, 2H, $C_{3,8}$-cyclobutyl protons); 1.21 (s, 6H, $C_{4,7}$-methyl protons).

m/e 526 (Molecular ion, 0.5%), 498 (15%), 258 (base peak).

Pyrolysis of 11,12-Bis(trifluoromethyl)-4,7-dimethyl-5,6-diphenylpentacyclo[8.2.2.$1^{4,7}$.$0^{2,9}$.$0^{3,8}$]pentadeca-5,11,13-trien-15-one (109)

The adduct (79 mg, 0.15 mmole) was placed in an n.m.r. tube and heated just above the melting point in a Wood's Metal bath at 200° for 15 minutes. A p.m.r. spectrum showed that pyrolysis was complete. Preparative scale t.l.c. (silica/2:1 benzene-cyclohexane) allowed isolation of *exo*-1,6-dimethyl-7,8-diphenyltricyclo[4.2.1.$0^{2,5}$]nona-3,7-dien-9-one (87) (36 mg, 77%). Recrystallization from *n*-hexane gave colourless needles, m.p. 133-134° (lit.[63] 136°).

λ_{max} 262 nm, ε 6200.

ν_{max} 704 s, 724 m, 760 m, 776 m, 848 m, 1287 m, 1771 s,

1790 m cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.4-6.9 (m, 10H, aromatic protons); 6.53 (s, 2H, $C_{3,4}$-olefinic protons); 3.16 (s, 2H, $C_{2,5}$-cyclobutyl protons); 1.22 (s, 6H, $C_{1,6}$-methyl protons).

m/e 312 (Molecular ion, 9%), 284 (base peak), 269 (62%), 254 (19%).

Photolyses of 11,12-Bis(trifluoromethyl)-4,7-dimethyl-5,6-diphenyl-tetracyclo[8.2.2.$1^{4,7}$.$0^{2,9}$.$0^{3,8}$]pentadeca-5,11,13-trien-15-one (109)

(a) Acetone solution, vycor filter

The ketone (26 mg, 0.05 mmole) was dissolved in acetone-d_6 (0.1 ml) in a thin quartz tube and irradiated at 0° (AH lamp, vycor filter). P.m.r. spectra recorded at intervals during the irradiation showed the formation and more gradual photolysis of *11,12-bis(trifluoromethyl)-4,7-dimethyl-5,6-diphenyltetracyclo-[8.2.2.$0^{2,9}$.$0^{3,8}$]tetradeca-4,6,11,13-tetraene* (110) (*vide infra*). The concentration of this product reached a maximum of 55% after 4 hours. After 8 hours, the solution contained 6% of unreacted ketone, 38% of tetraene (110) and 56% of 1,4-dimethyl-2,3-diphenylbenzene (77). No other products were detectable.

(b) Acetone solution, pyrex filter

The ketone (26 mg, 0.05 mmole) was dissolved in acetone-d_6 (0.1 ml) in a thin quartz tube and irradiated at 0° (AH lamp, pyrex filter) for periods up to 20 hours. P.m.r. spectra showed that no reaction had occurred.

(c) Ether solution, vycor filter

The ketone (53 mg, 0.1 mmole) and sodium-dried ether (1.0 ml) were placed in a thin quartz tube and irradiated at 0° (AH lamp, vycor filter). After 1 hour, a p.m.r. spectrum revealed the presence of the tetraene (110) (45%) and 1,4-dimethyl-2,3-diphenylbenzene (77) (30%). On irradiation for a further 4 hours, a p.m.r. spectrum showed that (77) was the only product present.

11,12-Bis(trifluoromethyl)-4,7-dimethyl-5,6-diphenyltetracyclo[8.2.2.$0^{2,9}$.$0^{3,8}$]tetradeca-4,6,11,13-tetraene (110)

A thin quartz tube containing 11,12-bis(trifluoromethyl)-4,7-dimethyl-5,6-diphenyltetracyclo[8.2.2.$1^{4,7}$.$0^{2,9}$.$0^{3,8}$]-pentadeca-5,11,13-trien-15-one (109) (263 mg, 0.5 mmole) in acetone (1.0 ml) was irradiated at 0° (AH lamp, vycor filter). Preliminary experiments (*vide supra*) using acetone-d_6 as solvent had shown that the concentration of the tetraene (110) reached a maximum after 4 hours of irradiation. Preparative scale t.l.c. (silica/3% ether in light petroleum, b.p. 60-80°) allowed separation of this product (137 mg, 55%) as a colourless glass. The product could not be obtained in the crystalline state.

λ_{max} 285 nm, ε 8200.

ν_{max} 703 ms, 722 ms, 1144 s, 1186 s, 1298 s, 1668 m cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.2-6.8 (m, 10H, aromatic protons); 6.69 (dd, 2H, $C_{13,14}$-olefinic protons); 4.23 (broad m, 2H, $C_{1,10}$-bridgehead protons); 2.27 (m, 4H, $C_{2,3,8,9}$-cyclobutyl protons); 1.46 (s, 6H, $C_{4,7}$-methyl protons).

m/e 498 (Molecular ion, 9%), 258 (base peak).

Adduct (111) of 11,12-Bis(trifluoromethyl)-4,7-dimethyl-5,6-diphenyltetracyclo[8.2.2.$0^{2,9}$.$0^{3,8}$]tetradeca-4,6,11,13-tetraene (110) and 4-Phenyl-1,2,4-triazoline-3,5-dione (48)

The tetraene (125 mg, 0.25 mmole) was dissolved in chloroform (5 ml) and the triazolinedione slowly added at room temperature until a slight pink colouration persisted. The solvent was removed under reduced pressure and the residue taken up in ethanol. After filtration, the solution was concentrated and cooled to give the crystalline *adduct*

(96 mg, 57%). Recrystallization from ethanol gave colourless needles, m.p. 206-208° (Found: C, 67.9; H, 4.5; N, 6.9; F, 16.5. $C_{38}H_{29}N_3F_6O_2$ requires C, 67.75; H, 4.3; N, 6.2; F, 16.9%).

λ_{max} 260 nm, ε 4600.

ν_{max} 692 m, 700 m, 725 m, 744 m, 1130 ms, 1189 ms, 1300 ms, 1673 w, 1716 s, 1769 m cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.53 (broad s, 5H, *N*-phenyl protons); 7.25-6.6 (m, aromatic protons and $C_{13,14}$-olefinic protons); 4.23 (broad m, 2H, $C_{1,10}$-bridgehead protons); 2.19 (broad s, $C_{2,3,8,9}$-cyclobutyl protons); 1.75 (s, 6H, $C_{4,7}$-methyl protons).

m/e 673 (Molecular ion, 69%), 498 (10%), 459 (6%), 407 (10%), 258 (base peak).

Photolysis of 11,12-Bis(trifluoromethyl)-4,7-dimethyl-5,6-diphenyltetracyclo[8.2.2.$0^{2,9}$.$0^{3,8}$]tetradeca-4,6,11,13-tetraene (110)

(a) Corex filter

A solution of the tetraene (125 mg, 0.25 mmole) in deuteriochloroform (0.5 ml) was placed in a thin quartz tube and irradiated at 0° under nitrogen (AH lamp, corex filter). After 2 hours, a p.m.r. spectrum showed that 32% conversion to 1,4-dimethyl-2,3-diphenylbenzene (77) had occurred. After 8 hours, conversion was 90%, but no other product was present.

(b) Pyrex filter

The tetraene (125 mg, 0.25 mmole) was irradiated as above using a pyrex filter. A p.m.r. spectrum after 8 hours showed that 60% conversion to (77) had occurred, but again, no other product was present.

5,6-Bis(trifluoromethyl)-1,10,13,14-tetrachloropentacyclo-[8.2.2.2^{4,7}.0^{2,9}.0^{3,8}]hexadeca-5,13,15-trien-11,12-dione (114)

7,8-Bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (108) (2.66 g, 0.01 mole), tetrachloro-*o*-benzoquinone (2.46 g, 0.01 mole) and benzene (40 ml) were heated under reflux for 48 hours.

On cooling, a first crop of crystalline *adduct* (3.06 g) was obtained. A further quantity (0.78 g) was obtained by concentration of the mother liquor to *ca.* 10 ml and addition of ether (10 ml). Both fractions were shown (by pyrolysis, *vide infra*) to have the same *exo*:*endo* isomer ratio of 3:4, and were subsequently combined (yield 75%). This isomer ratio was unaffected by further recrystallization* from benzene, which gave bright yellow needles, m.p. 192-193° (Found: C, 42.4; H, 1.7; Cl, 27.4; F, 22.2. $C_{18}H_8Cl_4F_6O_2$ requires C, 42.2; H, 1.6; Cl, 27.7; F, 22.3%).

λ_{max} ($CHCl_3$) 282, 438 nm, ε 725, 145.

ν_{max} 723 s, 1120-1190 s, 1304 s, 1566 m, 1573 m, 1675 m, 1762 s, 1772 s cm^{-1}.

P.m.r. (Acetone-d_6, δ p.p.m.) 6.93 (dd, 2H, $C_{15,16}$-olefinic protons); 4.50 (broad m, 2H, $C_{4,7}$-bridgehead protons); 2.82 (m, 2H, $C_{2,9}$-cyclobutyl protons); 2.50 and 2.20 (broad m, 2H, $C_{3,8}$-cyclobutyl protons of *endo* and *exo* isomers respectively).

m/e† 510 (Molecular ion, *ca.* 0.1%), 454 (14%), 240

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* Preparative scale t.l.c. on silica could not be used with these bridged α-diketones owing to their ease of hydration.

† See footnote page 100.

(base peak), 214 (15%), 171 (84%).

Formation of *exo*- and *endo*-1,6,9,10-Tetrachlorotricyclo-[4.2.2.$0^{2,5}$]deca-3,9-dien-7,8-dione (115) by Thermolysis of 5,6-Bis(trifluoromethyl)-1,10,13,14-tetrachloropentacyclo-[8.2.2.$2^{4,7}$.$0^{2,9}$.$0^{3,8}$]hexadeca-5,13,15-trien-11,12-dione (114)

A 3:4 mixture of the *exo* and *endo* adducts (205 mg, 0.4 mmole) was placed in an n.m.r. tube and heated just above the melting point in a Wood's Metal bath at 210°. The n.m.r. tube served as an air-condenser for condensation of the *o*-bis(trifluoromethyl)benzene (50) formed (b.p. 143°), which thus refluxed freely in the tube and served as an indication of the extent of reaction. After 5 minutes, a p.m.r. spectrum showed that reaction was complete. This procedure was repeated with another 2 x 205 mg of the starting material.*

The combined pyrolysates were then evacuated at room temperature (0.05 mm) to remove most of the *o*-bis(trifluoromethyl)benzene.

Several successive rapid crystallizations of the residue from sodium-dried *n*-hexane in the dark gave fine yellow needles of the pure *exo* isomer, m.p. 159-160° (Found: C, 40.4; H, 1.5; Cl, 47.4. $C_{10}H_4Cl_4O_2$ requires C, 40.3; H, 1.35; Cl, 47.6%). The *endo* isomer could not be obtained in the pure state.

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* This procedure avoided using larger tubes, which necessitated higher temperatures or longer reaction times, either of which led to excessive decomposition of the product.

exo isomer

λ_{max} 271, 435 nm, ε 2000, 250.

ν_{max} 744 m, 773 m, 1562 m, 1761 s cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 6.47 (s, 2H, $C_{3,4}$-olefinic protons); 3.83 (s, 2H, $C_{2,5}$-cyclobutyl protons).

*m/e** 296 (Molecular ion, 5%), 214 (16%), 205 (base peak), 170 (66%).

endo isomer

P.m.r. ($CDCl_3$, δ p.p.m.) 6.33 (s, 2H, $C_{3,4}$-olefinic protons); 3.60 (s, 2H, $C_{2,5}$-cyclobutyl protons).

1,6,9,10-Tetrachlorotricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene-[7,8-b]quinoxaline (117)

A mixture of *exo*- and *endo*-1,6,9,10-tetrachlorotricyclo-[4.2.2.$0^{2,5}$]deca-3,9-dien-7, 8 -dione (115) (3:4, 119 mg, 0.4 mmole), *o*-phenylenediamine (116) (44 mg, 0.4 mmole) and chloroform (3 ml) was heated under reflux in a water-bath for a few minutes. Almost immediate disappearance of the yellow colour of the α-diketones was observed.

The two *quinoxaline isomers* (126 mg, 85%) so obtained were not appreciably separated by preparative scale t.l.c. (silica/chloroform) or by recrystallization from ether which yielded colourless prisms, m.p. 158-160° (Found: C, 51.6; H, 2.1; N, 7.25; Cl, 38.0. $C_{16}H_8N_2Cl_4$ requires C, 51.9; H, 2.2; N, 7.6; Cl, 38.3%).

λ_{max} 318.5, 330 nm, ε 7500, 6600.

ν_{max} 768 s, 772 s, 801 ms, 820 ms, 961 ms, 1022 ms, 1570 m, 1586 m cm^{-1}.

P.m.r. (*exo* isomer, $CDCl_3$, δ p.p.m.) 8.4-7.8 (m (AA'BB'), 4H, aromatic protons), 6.15 (s, 2H, $C_{3,4}$-olefinic

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* See footnote page 100.

protons), 3.79 (s, 2H, $C_{2,5}$-cyclobutyl protons).

P.m.r. (*endo* isomer, $CDCl_3$, δ p.p.m.) 8.4-7.8 (m (AA'BB'), 4H, aromatic protons), 6.52 (s, 2H, $C_{3,4}$-olefinic protons), 3.43 (s, 2H, $C_{2,5}$-cyclobutyl protons).

*m/e** 368 (Molecular ion, 4%), 333 (base peak), 298 (38%), 52 (29%).

Photolysis of 5,6-Bis(trifluoromethyl)-1,10,13,14-tetrachloropentacyclo[8.2.2.$2^{4,7}$.$0^{2,9}$.$0^{3,8}$]hexadeca-5,13,15-trien-11,12-dione (114) - Preparation of 11,12-Bis(trifluoromethyl)-4,5,6,7-tetrachlorotetracyclo[8.2.2.$0^{2,9}$.$0^{3,8}$]tetradeca-4,6,11,13-tetraene (118), pentacyclo[8.2.2.$0^{2,9}$.$0^{3,8}$.$0^{4,7}$]tetradeca-5,11,13-triene (119), and tricyclo[8.2.2.$0^{2,9}$]tetradeca-3,5,7,11,13-pentaene (121)

The diketone (0.256-1.024 g, 0.5-2 mmole) was dissolved in dry THF or dry benzene (125 ml) under dry oxygen-free nitrogen and irradiated at 0° (AH lamp, pyrex filter) for the selected time.† The solution was then evaporated to dryness at room temperature under reduced pressure.

Repeated preparative scale t.l.c. (silica/1:1 carbon tetrachloride-light petroleum, b.p. 60-80°) allowed separation of the isomeric photoproducts together with 1,2,3,4-tetrachlorobenzene (120) (13-52 mg, 12%). 2,3-Bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene (112) could not be isolated.

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* See footnote page 100.

† The solution concentration and irradiation time were selected so as to maximize the amount of the particular photoproduct required in each run. This facilitated separation of the pure products. Product ratios and overall yields for concentrations in the range 1.5 to 8 g/l and periods up to 75 minutes are collected in Table 2 (page 57).

11,12-Bis(trifluoromethyl)-4,5,6,7-tetrachlorotetracyclo[8.2.2.$0^{2,9}$.$0^{3,8}$]tetradeca-4,6,11,13-tetraene (118) crystallized from light petroleum, b.p. 40-60°, as colourless prisms, m.p. 147-148° (Found: C, 42.1; H, 1.9; Cl, 31.4; F, 25.2. $C_{16}H_8Cl_4F_6$ requires C, 42.1; H, 1.8; Cl, 31.1; F, 25.0%).

λ_{max} 284 (infl.), 294, 304, 319 (infl.), ε 3050, 3600, 3350, 1700.

ν_{max} 723 s, 749 ms, 1026 s, 1123 s, 1145 s, 1183 s, 1289 s, 1303 s, 1610 s, 1660 m cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 6.73 (dd, 2H, $C_{13,14}$-olefinic protons); 4.35 (broad m, 2H, $C_{1,10}$-bridgehead protons); 2.62 (s, 2H, $C_{3,8}$-cyclobutyl protons); 2.62 (m, 2H, $C_{2,9}$-cyclobutyl protons).

*m/e** 454 (Molecular ion, 4%), 240 (89%), 214 (17%), 205 (20%), 171 (base peak).

11,12-Bis(trifluoromethyl)-4,5,6,7-tetrachloropentacyclo[8.2.2.$0^{2,9}$.$0^{3,8}$.$0^{4,7}$]tetradeca-5,11,13-triene (119) was obtained as colourless prisms, m.p. 162-163°, from light petroleum, b.p. 40-60° (Found: C, 41.95; H, 1.9; Cl, 30.7; F, 25.2. $C_{16}H_8Cl_4F_6$ requires C, 42.1; H, 1.8; Cl, 31.1; F, 25.0%).

The ultraviolet spectrum showed end absorption only.

ν_{max} 677 s, 719 s, 869 s, 1152 s, 1189 s, 1252 s, 1292 s, 1620 s, 1673 m cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 6.58 (dd, 2H, $C_{13,14}$-olefinic protons); 4.30 (broad m, 2H, $C_{1,10}$-bridgehead protons); 2.65 (m, 2H, $C_{2,9}$-cyclobutyl protons); 2.59 (broad s, 2H, $C_{3,8}$-cyclobutyl protons).

*m/e** 454 (Molecular ion, 0.5%), 240 (base peak), 214

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* See footnote page 100.

(19%), 205 (14%), 171 (97%).

11,12-Bis(trifluoromethyl)-4,5,6,7-tetrachlorotricyclo-[8.2.2.$0^{2,9}$]tetradeca-3,5,7,11,13-pentaene (121) was recrystallized from *n*-pentane (b.p. 36°) in order to prevent its facile isomerization to the pentacyclotetradecatetraene (118). The colourless prisms melted at 130-131° to a clear liquid which rapidly crystallized, and subsequently remelted at 145-146° [c.f. (118)] (Found: C, 41.8; H, 1.9; Cl, 30.8; F, 25.3. $C_{16}H_8Cl_4F_6$ requires C, 42.1; H, 1.8; Cl, 31.1; F, 25.0%).

λ_{max} 245 nm, ε 6800, together with tailing up to 300 nm (ε_{275} 1700, ε_{300} 340).

ν_{max} 720 s, 1010 m, 1102 ms, 1121 ms, 1189 s, 1296 s, 1309 s, 1586 m, 1682 w cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 6.77 (dd, 2H, $C_{13,14}$-olefinic protons); 5.75 (m, 2H, $C_{3,8}$-olefinic protons in cyclooctatriene ring); 4.18 (broad m, 2H, $C_{1,10}$-bridgehead protons); 2.99 (m, 2H, $C_{2,9}$-protons).

The mass spectrum of this product was identical to that of the pentacyclotetradecatetraene (118) (*vide supra*), probably due to thermal isomerization within the ion chamber.

Adduct (122) of 11,12-Bis(trifluoromethyl)-4,5,6,7-tetrachlorotetracyclo[8.2.2.$0^{2,9}$.$0^{3,8}$]tetradeca-4,6,11,13-tetraene (118) and 4-Phenyl-1,2,4-triazoline-3,5-dione (48)

The tetracyclotetradecatetraene (114 mg, 0.25 mmole) was dissolved in chloroform (5 ml) and the triazolinedione slowly added at room temperature until a slight pink colouration persisted. The *product* (129 mg, 82%) rapidly crystallized. Recrystallization from ethanol gave colourless needles, m.p. 202-203° (Found: C, 46.0; H, 2.3; N, 6.7; Cl, 23.1; F, 17.8. $C_{24}H_{13}N_3Cl_4F_6O_2$ requires

C, 45.7; H, 2.1; N, 6.7; Cl, 22.5; F, 18.1%).

λ_{max} 252 nm, ε 2660.

ν_{max} 697 m, 719 m, 730 m, 765 m, 1136 s, 1187 s, 1248 s, 1301 s, 1401 s, 1503 m, 1586 m, 1670 w, 1731 s, 1791 m cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.49 (broad s, 5H, *N*-phenyl protons); 6.79 (dd, 2H, $C_{13,14}$-olefinic protons); 4.30 (broad m, 2H, $C_{1,10}$-bridgehead protons); 2.63 (m, 4H, $C_{2,3,8,9}$-cyclobutyl protons).

*m/e** 629 (Molecular ion, 1%), 454 (14%), 240 (base peak), 214 (16%), 171 (80%), 119 (27%).

Pyrolysis of 11,12-Bis(trifluoromethyl)-4,5,6,7-tetrachloro-tetracyclo[8.2.2.$0^{2,9}$.$0^{3,8}$]tetradeca-4,6,11,13-tetraene (118)

The tetracyclotetradecatetraene (91 mg, 0.2 mmole) and deuteriochloroform (0.5 ml) were sealed into an n.m.r. tube and heated in an oil bath at 200° for 1½ hours, when pyrolysis was complete. Preparative scale t.l.c. (silica/light petroleum, b.p. 60-80°) gave 37 mg (78%) of a colourless oil, which was shown to be a 2:3 mixture of 1,2,3,8- and 1,2,3,4-tetrachlorocyclooctatetraene, (141) and (144) respectively, by comparison of its p.m.r. spectrum with authentic material (*vide infra*).

Photolysis of 11,12-Bis(trifluoromethyl)-4,5,6,7-tetrachloro-tetracyclo[8.2.2.$0^{2,9}$.$0^{3,8}$]tetradeca-4,6,11,13-tetraene (118)

The tetraene (114 mg, 0.25 mmole) was dissolved in deuteriochloroform (0.4 ml) in a thin quartz tube and irradiated at 0° under nitrogen (AH lamp, pyrex filter). The course of the reaction was followed by recording periodic p.m.r. spectra.

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* See footnote page 100.

After 9 hours, the mixture contained 1,2,3,4-tetrachlorobenzene [(120), 10%], 2,3-bis(trifluoromethyl)-bicyclo[2.2.2]octa-2,5,7-triene [(112), 10%], the tricyclotetradecapentaene [(121), 25%], the pentacyclotetradecatriene [(119), 45%] and unreacted tetraene [(118), 20%].

After 15 hours, (119) (40%) and (120) (10%) were the only products present.

Photolysis of 11,12-Bis(trifluoromethyl)-4,5,6,7-tetrachlorotricyclo[8.2.2.$0^{2,9}$]tetradeca-3,5,7,11,13-pentaene (121)

The tricyclotetradecapentaene (46 mg, 0.1 mmole) in deuteriochloroform (0.4 ml) in a thin quartz tube was irradiated at 0° (AH lamp, pyrex filter). After 2 hrs, 40% of the starting material had reacted, while after 4 hours, only 35% remained. No products could be seen in p.m.r. spectra of the photolysate, suggesting that complete break-up of the cyclooctatriene derivative had occurred.

Thermal Conversion of 11,12-Bis(trifluoromethyl)-4,5,6,7-tetrachlorotricyclo[8.2.2.$0^{2,9}$]tetradeca-3,5,7,11,13-pentaene (121), to 11,12-Bis(trifluoromethyl)-4,5,6,7-tetrachlorotetracyclo[8.2.2.$0^{2,9}.0^{3,8}$]tetradeca-4,6,11,13-tetraene (118)

The tricyclotetradecapentaene (46 mg, 0.1 mmole) and deuteriochloroform (0.4 ml) were sealed into an n.m.r. tube and heated in an oil bath at 80°. P.m.r. spectra showed that conversion after 15 minutes was 32%, after 30 minutes, 54% and after 45 minutes, 68%. These figures correspond to a first-order half-life of 27 minutes at this temperature.

The isomerization was rapid at 100°, and at the melting point of (121) (130°), was complete within a few seconds.

The product, 11,12-bis(trifluoromethyl)-4,5,6,7-tetrachlorotetracyclo[8.2.2.$0^{2,9}$.$0^{3,8}$]tetradeca-4,6,11,13-tetraene (118), was shown to be identical to that previously described by comparison of p.m.r. and u.v. spectra.

Thermal Isomerization of 11,12-Bis(trifluoromethyl)-4,5,6,7-tetrachloropentacyclo[8.2.2.$0^{2,9}$.$0^{3,8}$.$0^{4,7}$]tetradeca-5,11,13-triene (119) to 11,12-Bis(trifluoromethyl)-4,5,6,7-tetrachloro-tetracyclo[8.2.2.$0^{2,9}$.$0^{3,8}$]tetradeca-4,6,11,13-tetraene (118)

Small samples (*ca.* 2-3 mg) of the pentacyclotetradeca-triene were weighed out accurately, dissolved in chloroform (2.00 ml) and sealed into 5 ml ampoules. After heating in an oil bath at 140° for periods up to 1 hour, the ampoules were opened, 1.00 ml taken, diluted to 5.00 ml and the u.v. spectrum recorded. From the progressive increase in absorption at 296 nm due to the product, the % conversion was calculated.

Conversion was 22% after 16 minutes, 41% after 32 minutes and 55% after 50 minutes. These figures correspond to a first-order half-life of 44 minutes at this temperature.

At 200°, complete isomerization occurred within 15 minutes.

The product, 11,12-bis(trifluoromethyl)-4,5,6,7-tetrachlorotetracyclo[8.2.2.$0^{2,9}$.$0^{3,8}$]tetradeca-4,6,11,13-tetraene (118) was shown to be identical to that described earlier by comparison of p.m.r. and u.v. spectra.

5,6-*cis*-Dimethoxycarbonyl-1,10,13,14-tetrachloropentacyclo-[8.2.2.$2^{4,7}$.$0^{2,9}$.$0^{3,8}$]hexadeca-13,15-dien-11,12-dione (127)

7,8-*cis*-Dimethoxycarbonyltricyclo[4.2.2.$0^{2,5}$]deca-3,9-diene (125) (2.48 g, 1 mmole), tetrachloro-*o*-benzoquinone (2.46 g, 1 mmole) and benzene (20 ml) were heated under reflux for 12 hours. On cooling, a first crop of crystalline *adduct* (2.72 g) was obtained. A

further quantity (1.60 g, combined yield 87%) was obtained by concentration of the mother liquor to 10 ml and addition of ether (10 ml). Recrystallization from benzene gave bright yellow crystals, m.p. 278-280° with decomposition (Found: C, 48.8; H, 3.4; Cl, 28.1. $C_{20}H_{16}Cl_4O_6$ requires C, 48.6; H, 3.3; Cl, 28.7%).

λ_{max} ($CHCl_3$) 272, 438 nm, ε 2240, 310.

ν_{max} 734 m, 751 m, 1180 s, 1210 s, 1445 ms, 1559 ms, 1748 s, 1760 s cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 6.62 (dd, 2H, $C_{15,16}$-olefinic protons); 3.65 (s, 6H, *O*-methyl protons); 3.17 (broad m, 2H, $C_{4,7}$-bridgehead protons); 2.89 (broad s, 2H, $C_{5,6}$-protons); 2.63 (m, 2H, $C_{2,9}$-cyclobutyl protons); 1.98 (broad m, 2H, $C_{3,8}$-cyclobutyl protons).

*m/e** 492 (Molecular ion, 1%), 436 (2%), 190 (23%), 163 (24%), 131 (20%), 113 (12%), 78 (base peak).

Photolysis of 5,6-*cis*-Dimethoxycarbonyl-1,10,13,14-tetrachloropentacyclo[8.2.2.$2^{4,7}$.$0^{2,9}$.$0^{3,8}$]hexadeca-13,15-dien-11,12-dione (127) - Preparation of 2,3-*cis*-Dimethoxycarbonylbicyclo[2.2.2]octa-5,7-diene (131)

The α-diketone (494 mg, 1 mmole) was dissolved in dry benzene (125 ml) and irradiated at 0° in a nitrogen atmosphere (AH lamp, pyrex filter) for 6 hours. Removal of the solvent under reduced pressure at room temperature left a yellow oil. Preparative scale t.l.c. (silica/1:1 ether - light petroleum, b.p. 60-80°) was employed to separate the photoproducts.

1,2,3,4-Tetrachlorobenzene (140 mg, 65%) was shown to be identical with authentic material.† *2,3-*cis*-Dimethoxy-*

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* See footnote page 100.

† Kindly provided by Dr. W.S. Wilson.

carbonylbicyclo[2.2.2]*octa-5,7-diene* (144 mg, 65%) was obtained as a colourless oil, which slowly crystallized after thorough drying at room temperature (0.1 mm). The m.p. was 54-55° (Found: C, 64.6; H, 6.1. $C_{12}H_{14}O_4$ requires C, 64.85; H, 6.35%).

Apart from end absorption (λ_{max}<225 nm), the u.v. spectrum of the dihydrobarrelene showed only very weak absorption in the near u.v. region (ε_{275} 30, ε_{300} 15).

ν_{max} 728 ms, 1045 ms, 1165 s, 1203 s, 1258 ms, 1433 ms, 1748 s cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 6.6-6.4 (2 x q, 4H, $C_{5,6,7,8}$-olefinic protons); 3.93 (m, 2H, $C_{1,4}$-bridgehead protons); 3.66 (s, 6H, *O*-methyl protons); 2.95 (broad s, 2H, $C_{2,3}$-protons).

m/e 222 (Molecular ion, 1%), 190 (9%), 131 (15%), 113 (74%), 78 (base peak).

11,12-cis-*Dimethoxycarbonyl-4,5,6,7-tetrachlorotricyclo-*[*8.2.2.*$0^{2,9}$]*tetradeca-3,5,7,13-tetraene* (130) (54 mg, 12%) formed colourless prisms, m.p. 197-199°, from ether (Found: C, 49.2; H, 3.5; Cl, 32.3. $C_{18}H_{16}Cl_4O_4$ requires C, 49.35; H, 3.7; Cl, 32.4%).

λ_{max} 245 nm, ε 3100, together with tailing up to 300 nm, (ε_{275} 810, ε_{300} 110).

ν_{max} 1210 ms, 1440 m, 1583 mw, 1740 s cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 6.59 (dd, 2H, $C_{13,14}$-olefinic protons); 5.82 (m, 2H, $C_{3,8}$-olefinic protons in cyclooctatriene ring); 3.67 (s, 6H, *O*-methyl protons); 3.20 (broad s, 2H, $C_{11,12}$-protons); 3.1-2.9 (m, 4H, $C_{1,10}$-bridgehead protons and $C_{2,9}$-protons).

m/e[*] 436 (Molecular ion, 1%), 214 (5%), 190 (19%), 163 (26%), 131 (38%), 78 (base peak).

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* See footnote page 100.

Irradiation of the α-diketone in more concentrated solution (0.99 g, 2 mmole, in 125 ml benzene) for a shorter period (2 hours) gave 1,2,3,4-tetrachlorobenzene (120) (116 mg, 27%), the dihydrobarrelene (131) (115 mg, 26%), and crystalline material (445 mg, 51%) thought to contain (128) and (129). Although very difficult to separate, a sample (100 mg, 11%) of the latter, *11,12*-cis-*dimethoxycarbonyl-4,5,6,7-tetrachloropentacyclo*[*8.2.2.*$0^{2,9}$*.*$0^{3,8}$*.*$0^{4,7}$]*tetradeca-5,13-diene* (129) was obtained as colourless needles, m.p. 157-158°, from *n*-hexane (Found: C, 49.7; H, 3.6; Cl, 32.1. $C_{18}H_{16}Cl_4O_4$ requires C, 49.35; H, 3.7; Cl, 32.4%).

The u.v. spectrum showed end absorption only.

ν_{max} 1167 ms, 1210 ms, 1380 s, 1619 m, 1743 s cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 6.49 (dd, 2H, $C_{13,14}$-olefinic protons); 3.67 (s, 6H, *O*-methyl protons); 3.10 (broad m, 2H, $C_{1,10}$-bridgehead protons); 3.07 (broad s, 2H, $C_{11,12}$-protons); 2.66 (broad s, 4H, $C_{2,3,8,9}$-cyclobutyl protons).

*m/e** 436 (Molecular ion, *ca.* 0.5%), 214 (5%), 190 (23%), 163 (32%), 131 (44%), 78 (base peak).

Thermolysis of 2,3-*cis*-Dimethoxycarbonylbicyclo[2.2.2]octa-5,7-diene (131)

The bicyclooctadiene (22 mg, 0.1 mmole) in deuteriochloroform (0.4 ml) was heated in an oil-bath at 60° while the cycloreversion to benzene and dimethyl maleate was observed by p.m.r. spectroscopy. Conversion to these products amounted to 12% after 1 hour, 20% after 2 hours, 37% after 4 hours, 50% after 6 hours and 60.5% after 8 hours. These figures correspond well to a first-order half-life of 6 hours at this temperature. Complete reaction occurred overnight at 75°; evaporation of the

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* See footnote page 100.

solution left a colourless oil (14 mg, 100%) which was shown to be dimethyl maleate by comparison of p.m.r., i.r. and mass spectra with an authentic sample.

Photolysis of *exo*- and *endo*-1,6,9,10-Tetrachlorotricyclo-[4.2.2.$0^{2,5}$]deca-3,9-dien-7,8-dione (115) - Preparation of 2,3,4,5-Tetrachlorobicyclo[4.2.0]octa-2,4,7-triene (139)

The 3:4 mixture of *exo*- and *endo*-5,6-bis(trifluoromethyl)-1,10,13,14-tetrachloropentacyclo[8.2.2.$2^{4,7}$.$0^{2,9}$.$0^{3,8}$]-hexadeca-5,13,15-trien-11,12-dione (114) (154 mg, 0.3 mmole) was placed in a thin quartz tube and heated in a Wood's Metal bath at 210° for 5 minutes according to the procedure already described (see page 121).

Deuteriochloroform (0.5 ml) was then added, and the bright yellow solution irradiated* at 0° under nitrogen (AH lamp, pyrex filter). After 1 hour, the vigorous carbon monoxide evolution had ceased, and a p.m.r. spectrum confirmed that none of the diketone remained.

Preparative scale t.l.c. (silica/light petroleum, b.p. 60-80°) allowed separation of the *biCOT* (59 mg, 82%) as an oil which slowly crystallized when stored at 0°. The colourless crystals had m.p. 38-39° (Found:† C, 39.6; H, 1.65; Cl, 56.7. $C_8H_4Cl_4$ requires C, 39.7; H, 1.7; Cl, 58.6%).

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* *o*-Bis(trifluoromethyl)benzene, the other pyrolysis product, had no adverse effect on the photolysis, and was easily separated at the later stage.

† Chlorine analyses of this and related tetrachloro-C_8 hydrocarbons were consistently 1-2% low, though C and H analyses were usually satisfactory. This was thought to be due to partial volatilization and consequent incomplete combustion during the Cl determination.

λ_{max} 286 (infl.), 296.5, 308, 321 (infl.) nm, ε 3700, 4600, 4250, 2100.

ν_{max} 751 vs, 1101 ms, 1210 ms, 1610 s cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 6.26 (s, 2H, $C_{7,8}$-olefinic protons); 3.94 (s, 2H, $C_{1,6}$-cyclobutyl protons).

*m/e** 239.9070 (Molecular ion, 25%, $C_8H_4Cl_4$ requires 239.9067), 214 (50%), 205 (base peak), 170 (97%).

N-Phenyl-1,6,9,10-tetrachloro-7,8-diazatricyclo[4.2.2.$0^{2,5}$]-deca-3,9-diene-7,8-dicarboximide (140)

2,3,4,5-Tetrachloro-biCOT (139) (73 mg, 0.3 mmole) was dissolved in chloroform (5 ml) and 4-phenyl-1,2,4-triazoline-3,5-dione (48) slowly added at room temperature until no further decolourization occurred. Preparative scale t.l.c. (silica/chloroform) allowed isolation of the *adduct* (103 mg, 82%). Recrystallization from ethanol gave colourless prisms, which decomposed without melting above 175° (Found: C, 45.1; H, 2.4; N, 10.0; Cl, 33.3. $C_{16}H_9N_3Cl_4O_2.\frac{1}{2}H_2O$ requires C, 45.1; H, 2.4; N, 9.9; Cl, 33.3%).

λ_{max} 251 nm, ε 3300.

ν_{max} 708 ms, 775 ms, 1038 m, 1172 m, 1402 s, 1495 w, 1507 m, 1582 m, 1737 s, 1789 m cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.47 (s, 5H, *N*-phenyl protons); 6.34 (s, 2H, $C_{3,4}$-olefinic protons); 3.75 (s, 2H, $C_{2,5}$-cyclobutyl protons).

*m/e** 415 (Molecular ion, 10%), 240 (60%), 214 (19%), 205 (base peak), 170 (44%), 119 (37%).

Pyrolysis of the 4-Phenyl-1,2,4-triazoline-3,5-dione Adduct (122)

The adduct (158 mg, 0.25 mmole) and deuteriochloroform

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* See footnote page 100.

(0.6 ml) were sealed into an n.m.r. tube and heated in an oil bath at 210°. P.m.r. spectra showed that 25% reaction had occurred after 30 minutes, and essentially complete pyrolysis had occurred after 1½ hours. The only identifiable products were *o*-bis(trifluoromethyl)benzene (50) and 1,2,3,8- and 1,2,3,4-tetrachloro-COT [(141) and (144)] (*vide infra*). The COTs were apparently formed by cyclo-reversion of the initially formed *N*-phenyl-1,6,9,10-tetrachloro-7,8-diazatricyclo[4.2.2.$0^{2,5}$]deca-3,9-diene-7,8-dicarboximide (140) (*vide supra*).

Thermal Isomerization of 2,3,4,5-Tetrachlorobicyclo[4.2.0]-octa-2,4,7-triene (139) to 1,2,3,8-Tetrachlorocyclo-octatetraene (141)

(a) Kinetic Study

The biCOT (24 mg, 0.1 mmole) and deuteriochloroform (0.4 ml) were sealed into an n.m.r. tube and heated in an oil bath at 60°. P.m.r. spectra recorded at 10 minute intervals, showed that 37, 60 and 75% conversion had occurred after 10, 20 and 30 minutes respectively. These figures correspond to a first-order half-life of 15 minutes at this temperature.

(b) Preparative Scale

The biCOT (72 mg, 0.3 mmole) and deuteriochloroform (0.4 ml) were sealed into an n.m.r. tube and heated in an oil bath at 60° for 3 hours. A p.m.r. spectrum confirmed that isomerization was complete. Evaporation to dryness at room temperature under reduced pressure (12 mm) gave *1,2,3,8-tetrachloro-COT* (72 mg, 100%) as a colourless crystalline solid, m.p. 55-57° (Found*: C, 39.7; H, 1.7;

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* See footnote page 132.

Cl, 57.0, 56.3. $C_8H_4Cl_4$ requires C, 39.7; H, 1.7; Cl, 58.6%).

λ_{max} 237.5 nm, ε 4200, together with tailing up to 350 nm (ε_{300} 290, ε_{325} 130).

ν_{max} 703 m, 713 s, 857 m, 1136 ms, 1601 m cm^{-1}.

The p.m.r. spectrum ($CDCl_3$) showed two symmetrical multiplets centred at 6.32 and 6.14 δ, of equal intensity.

*m/e** 239.9077 (Molecular ion, 10%, $C_8H_4Cl_4$ requires 239.9067), 214 (4%), 205 (98%), 180 (4%), 170 (base peak), 146 (5%), 135 (14%).

N-Phenyl-2,3,4,5-tetrachloro-7,8-diazatricyclo[4.2.2.$0^{2,5}$]deca-3,9-diene-7,8-dicarboximide (143)

1,2,3,8-Tetrachloro-COT (141) (61 mg, 0.25 mmole) was dissolved in chloroform (5 ml), and 4-phenyl-1,2,4-triazoline-3,5-dione (48) slowly added at room temperature. Reaction with the first few milligrams of (48) was rapid, then much slower as conversion of the COT to 1,6,7,8-tetrachloro-biCOT (142) took place. Complete reaction required 24 hours.

Preparative scale t.l.c. (silica/chloroform) allowed isolation of the *adduct* (96 mg, 92%). Recrystallization from ethanol gave colourless crystals, which decomposed without melting on heating above 270° (Found: C, 45.8; H, 2.3; N, 10.2; Cl, 34.3. $C_{16}H_9N_3Cl_4O_2$ requires C, 46.1; H, 2.2; N, 10.1; Cl, 34.0%).

λ_{max} 264 nm, ε 2100.

ν_{max} 690 ms, 702 ms, 731 s, 769 m, 779 m, 897 m, 1140 ms, 1193 s, 1424 s, 1508 m, 1634 m, 1715 s, 1789 ms cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.50 (s, 5H, *N*-phenyl protons); 6.57 (dd, 2H, $C_{9,10}$-olefinic protons); 5.25 (dd, 2H, $C_{1,6}$-bridgehead protons adjacent to nitrogen).

*m/e** 415 (Molecular ion, 51%), 380 (24%), 296 (12%),

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* See footnote page 100.

254 (21%), 227 (99%), 119 (base peak), 80 (51%).

Thermal Isomerization of 1,2,3,8-Tetrachlorocyclooctatetraene (141) to 1,2,3,4-Tetrachlorocyclooctatetraene (144)

1,2,3,8-Tetrachloro-COT (36 mg, 0.15 mmole) and deuteriochloroform (0.4 ml) were sealed into an n.m.r. tube and heated in an oil bath at temperatures up to 140° for 10 minutes. P.m.r. spectra showed that no change had occurred to this point.

On heating at 150°, steady conversion to *1,2,3,4-tetrachloro-COT* was observed, 50% conversion being achieved after 4 hours. After 6 hours, an equilibrium was attained, the ratio of isomers being 2:1 [(144) predominating]. The two isomers could not be separated by t.l.c. (silica/light petroleum, b.p. 60-80°) or by g.l.c. (6' x 3/8" column of 10% SE30 on Embacel, 150°, retention time 9.5 mins).

The p.m.r. spectrum ($CDCl_3$) of (144) showed a single sharp singlet at 6.23 δ.

N-Phenyl-1,2,3,4-tetrachloro-7,8-diazatricyclo[4.2.2.$0^{2,5}$]-deca-3,9-diene-7,8-dicarboximide (146)

A 1:2 mixture (*vide supra*) of 1,2,3,8- and 1,2,3,4-tetrachloro-COT [(141) and (144)] (36 mg, 0.15 mmole) was dissolved in chloroform (2 ml) and allowed to react with 4-phenyl-1,2,4-triazoline-3,5-dione (48) at room temperature. The initial reaction was rapid, but 24 hours was required for complete reaction as conversion of the COTs to the isomeric 1,6,7,8- and 1,2,7,8-tetrachloro-biCOTs [(142) and (145)] was slow.

Preparative scale t.l.c. (silica/chloroform) allowed

partial separation* of the required *adduct* (23 mg, 38%). Recrystallization from ethanol gave colourless prisms, which decomposed without melting above 225° (Found: C, 45.45; H, 2.5; N, 9.65; Cl, 33.6. $C_{16}H_9N_3Cl_4O_2.\frac{1}{4}H_2O$ requires C, 45.6; H, 2.3; N, 10.0; Cl, 33.6%).

λ_{max} 261 nm, ε 2050.

ν_{max} 679 m, 726 m, 768 m, 1410 ms, 1499 m, 1622 m, 1729 s, 1787 m cm^{-1}.

P.m.r.($CDCl_3$, δ p.p.m.) 7.52 (s, 5H, *N*-phenyl protons); 6.55 (m, 2H, $C_{9,10}$-olefinic protons); 5.30 (m, 1H, C_6-bridgehead proton); 3.86 (m, C_5-cyclobutyl proton).

m/e† 415 (Molecular ion, 64%), 380 (base peak), 345 (13%), 296 (10%), 261 (20%), 119 (37%).

Irradiation of 2,3,4,5-Tetrachlorobicyclo[4.2.0]octa-2,4,7-triene (139)

The biCOT (48 mg, 0.2 mmole) was dissolved in deuteriochloroform (0.4 ml) in a quartz n.m.r. tube and irradiated at 0° (AH lamp, pyrex filter). After 4 hours, 20% conversion to photoproducts had occurred, and irradiation was stopped at this point.

The products, 1,2,3,8- and 1,2,3,4-tetrachloro-COT [(141) and (144)] (1:1, 10 mg, 100% from unrecovered biCOT) were separated from unreacted starting material (38 mg), by preparative scale t.l.c. (silica/light petroleum, b.p. 60-80°), and were identified by their characteristic p.m.r. spectra (*vide supra*). No other photoproducts were detected.

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* A second fraction (30 mg, 50%) contained *N*-phenyl-2,3,4,5- and 1,2,3,4-tetrachloro-7,8-diazatricyclo[4.2.2.$0^{2,5}$]deca-3,9-diene-7,8-dicarboximide [(143) and (146)].

† See footnote page 100.

Irradiation of 1,2,3,8-Tetrachlorocyclooctatetraene (141)

The COT (24 mg, 0.1 mmole) was dissolved in deuteriochloroform in a thin quartz tube and irradiated at 0° (AH lamp, pyrex filter) for 3 hours. A p.m.r. spectrum showed that 60% conversion to 1,2,3,4-tetrachloro-COT (144) had occurred. No change occurred on further irradiation, showing that a photostationary state had been reached. No other products were detected.

2,3,4,5-Tetrachlorobicyclo[4.2.0]octa-2,4-diene (147)

10% Palladium on charcoal (2 mg) was suspended in methanol (20 ml) and saturated with hydrogen at atmospheric pressure. Freshly prepared 2,3,4,5-tetrachloro-biCOT (139) (61 mg, 0.25 mmole) was then added, and the mixture stirred vigorously at room temperature until 1:1 equivalents of hydrogen had been absorbed. The mixture was then filtered through cellulose powder to remove the catalyst, poured into cold water and extracted with *n*-pentane (3 x 25 ml). After washing with water (2 x 25 ml), the extracts were dried over anhydrous magnesium sulphate and evaporated to dryness at room temperature. The p.m.r. spectrum was checked to ensure that no unreacted biCOT remained.

Preparative scale t.l.c. (silica/light petroleum, b.p. 60-80°) followed by distillation (40°, 0.05 mm) allowed isolation of *2,3,4,5-tetrachlorobicyclo[4.2.0]octa-2,4-diene* (40 mg, 65%) as a colourless oil, which slowly crystallized when stored at 0°. The m.p. was *ca.* 25° (Found : C, 39.3; H, 2.6; Cl, 58.1. $C_8H_6Cl_4$ requires C, 39.4; H, 2.5; Cl, 58.1%).

λ_{max} 288 (infl.), 297.5, 307.5 (infl.), 323 (infl.) nm, ε 4050, 5100, 4150, 1850.

ν_{max} 709 s, 1110 m, 1205 m, 1610 s cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 3.58 (m, 2H, $C_{1,6}$-allylic cyclobutyl protons); 2.54 (m, 4H, $C_{7,8}$-cyclobutyl protons).

m/e * 242 (Molecular ion, 17%), 214 (base peak).

N-Phenyl-1,6,9,10-tetrachloro-7,8-diazatricyclo[4.2.2.$0^{2,5}$]-dec-9-ene-7,8-dicarboximide (148)

2,3,4,5-Tetrachlorobicyclo[4.2.0]octa-2,4-diene (147) (29 mg, 0.12 mmole) was dissolved in chloroform (2 ml) and allowed to react with an excess of 4-phenyl-1,2,4-triazoline-3,5-dione (48) at room temperature. Preparative scale t.l.c. (silica/chloroform) was used to isolate the *adduct* (47 mg, 94%). Recrystallization from ethanol yielded colourless prisms, m.p. 143-144° (Found: C, 45.4; H, 2.5; N, 9.7; Cl, 33.8. $C_{16}H_{11}N_3Cl_4O_2.\frac{1}{4}H_2O$ requires C, 45.4; H, 2.7; N, 9.9; Cl, 33.5%).

λ_{max} 250 (infl.) nm, ε 2800.

ν_{max} 694 m, 740 ms, 804 m, 1048 ms, 1173 ms, 1403 s, 1503 m, 1580 m, 1740 s, 1789 m cm^{-1}.

P.m.r. ($CDCl_3$, δ p.p.m.) 7.48 (s, 5H, *N*-phenyl protons); 3.6-3.2 (m, 2H, $C_{2,5}$-cyclobutyl protons); 2.5-1.6 (m, 4H, $C_{3,4}$-cyclobutyl protons).

m/e * 417 (Molecular ion, 4%), 242 (43%), 214 (base peak), 119 (24%).

Irradiation of 2,3,4,5-Tetrachlorobicyclo[4.2.0]octa-2,4-diene (147)

The diene (49 mg, 0.2 mmole) was dissolved in deuteriochloroform (0.5 ml) in a thin quartz tube and irradiated at 0° (AH lamp, pyrex filter). After 5 hours, a p.m.r. spectrum showed that reaction was complete, and the products were

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* See footnote page 100.

separated by preparative scale t.l.c. (silica/light petroleum, b.p. 60-80°).

1,2,3,4-Tetrachlorobenzene (120) (9.5 mg, 22%) was identified by comparison of its u.v. and i.r. spectra with those of an authentic sample. Other products were not identified.

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